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Modeling of Stripper Configurations for CO_2 Capture using Aqueous Piperazine

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Modeling of Stripper Configurations for CO_2 Capture using Aqueous Piperazine

by

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Dedication

To my family

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Abstract

Stripper configurations and Process Modeling for CO_2 capture using Piperazine

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This thesis seeks to improve the economic viability of carbon capture process by reducing the energy requirement of amine scrubbing technology. High steam requirement for solvent regeneration in this technology can be reduced by improvements in the regeneration process. Solvent models based on experimental results have been created by previous researchers and are available for simulation and process modeling in Aspen Plus®. Standard process modeling specifications are developed and multiple regeneration processes are compared for piperazine (a cyclic diamine) in Chapter 2. The configurations were optimized to identify optimal operating conditions for energy performance. These processes utilize methods of better heat recovery and effective separation and show 2 to 8% improvement in energy requirement as compared to conventional absorber-stripper configuration. The best configuration is the interheated stripper which requires equivalent work of 29.9 kJ/mol CO_2 compared to 32.6 kJ/mol CO_2 for the simple stripper. The Fawkes and Independence solvent models were used for modeling and simulation.

A new regeneration configuration called the advanced flash stripper (patent pending) was developed and simulated using the Independence model. Multiple complex levels of the process were simulated and results show more than 10% improvement in energy performance. Multiple cases of operating conditions and process specifications were simulated and the best case requires equivalent work of 29 kJ/mol CO_2.

This work also includes modeling and simulation of pilot plant campaigns carried out for demonstration of a piperazine with a 2-stage flash on at 1 tpd CO_2. Reconciliation of data was done in Aspen Plus for solvent model validation. The solvent model predicted results consistent with the measured values. A systematic error of approximately +5% was found in the rich CO_2, that can be attributed to laboratory measurement errors, instrument measurement errors, and standard deviation in solvent model data.

Stripper Modeling for CO_2 capture from natural gas combustion was done under a project by TOTAL through the Process Science and Technology Center. Two configurations were simulated for each of three flue gas conditions (corresponding to 3%, 6% and 9% CO_2). Best cases for the three conditions of flue gas require 34.9, 33.1 and 31.6 kJ/mol CO_2.

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Chapter 1: Introduction

This chapter introduces the amine scrubbing technology for CO_2 capture and the importance of stripper modeling with respect to this technology. The basic process of amine scrubbing for CO_2 capture is an established technology with the first patent dating to 1930 (Bottoms, 1930). The technology has been in use for decades in acid gas treatment and is the preferred technology for post combustion capture from power plants.

The high energy requirement for amine scrubbing is one of the major obstacles toward its implementation on a commercial scale. Although substantially better than competing technologies, the energy required for solvent regeneration and CO_2 compression is high (Rochelle, 2009). Early estimates show that its implementation on a coal fired power plant could reduce the power plant output by as much as 20 to 30% (Fisher, 2007)

Process modeling of the solvent regeneration helps in evaluating and identifying new configurations with reduced energy. This chapter summarizes the importance and expected benefit of stripper modeling. A review of previous work has been done and research objectives are defined.

1.1 POST COMBUSTION CO_2 CAPTURE AND AMINE SCRUBBING

Atmospheric CO_2, measured at Mauna Loa Observatory has reached a level of 395 ppm, which is substantially higher than 280 ppm in pre-industrial era (Tans, 2013). The increasing CO_2, due to anthropogenic emissions in the atmosphere, is considered to be prime reason of an increasing trend of global temperature (Solomon et al., 2009). In 2010, 43% of these emissions were from combustion of coal, making the coal fired power plant the largest single point source of CO_2 emissions (IEA, 2012). Coal power accounts for 42% of electricity generation in the United States (EIA, 2013) and 40.5% of the world

(World Bank, 2013). Due to this large dependence on coal, any attempt to significantly reduce the CO_2 emissions will have to include post combustion carbon capture from existing coal fired power plants.

CO_2 absorption using amine scrubbing is an established technology for acid gas application and is under investigation for use in post combustion. The process consists of countercurrent contact of flue gas and an amine solvent in an absorber. The amine solvent absorbs CO_2 from the flue gas by undergoing an exothermic reversible reaction. For example, MEA (monoethanolamine, a primary amine) undergoes the following reaction.

$$OH - CH_2 - CH_2 - NH_2 + CO_2 \rightleftharpoons OH - CH_2 - CH_2 - NH_3^+ + OH - CH_2 - CH_2 - NHCOO^-$$

The rich solvent is regenerated in the stripping system where the solvent is heated to reverse the reaction. Heat is recovered from the hot lean solvent in a cross exchanger and is pumped back to the absorber for reuse. The cyclic process is shown in Figure 1.

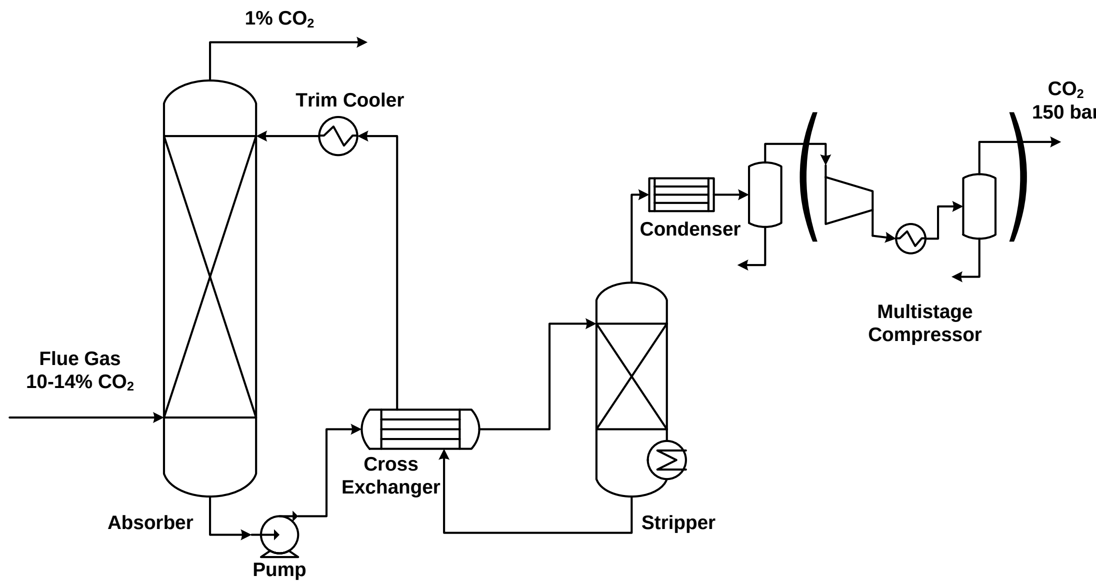

Figure 1: Amine Scrubbing Process

1.2 STRIPPER MODELING

The process has two major energy requirements, heating requirement in the stripper and compression work in the multistage compressor. CO_2 is required to have a final discharge pressure of few hundred bars for geologic sequestration (Benson et al., 2008). Modeling of the stripping section of the process helps in evaluating and quantifying this energy requirement. Experimental results are used to prepare thermodynamic and kinetic models for various solvents. Stripper modeling, based on these solvent models is used for evaluating and optimizing energy performance of the process at different operating conditions.

A conventional stripper can also be replaced by a more complex regeneration system which gives better performance. A more complex system decreases the energy requirement of the system by doing more reversible separation at multiple pressure and temperature levels. Most of advanced stripper configurations aim at achieving reduced heat duty in the stripper and elevated pressure of product to reduce compression work

(Van Wagener, 2011). Stripper modeling of such advanced configurations is used for evaluating and creating conceptual designs for these complex configurations.

Stripper modeling is also useful for validation of the solvent model on a pilot scale. Data from pilot scale tests is reconciled using stripper models and the solvent models are validated and improved using reconciliation of model and pilot results.

1.3 Prior Work

Most of the prior work on stripper modeling and new stripper configurations has focused on monoethanolamine solvent. In the last few years, piperazine, a cyclic secondary amine, has gained considerable attention of researchers and is the primary solvent choice for the application (Rochelle et al., 2011). Piperazine has high absorption rate (Dugas et al., 2009), good capacity (Freeman et al., 2009), and very good resistance to thermal and oxidative degradation (Freeman et al., 2010). Figure 2 shows the structure of piperazine solvent.

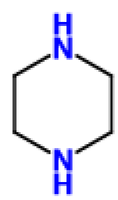

Figure 2: Piperazine

Much of the early work had been focused on performance modeling, simulation and demonstration of CO_2 removal systems consisting of conventional absorber and stripper system. Some early work used monoethanolamine (MEA) with equilibrium reactions model to simulate post combustion operating conditions in Aspen Plus® and calculate the energy requirement (Desideri et al., 1999). Modeling and demonstration of the amine scrubbing process has also been of commercial interest and has been an important topic of research in industry (Steinberg et al., 1984). Many of these studies include pilot plant testing and development of technology while identifying the areas of cost and energy savings (Suda et al., 1992). Most of the earlier modeling and simulation work was done on the entire system of absorber, stripper and compressor. However, as more complex solvent models were built, the system was usually simulated in individual components of absorber and stripper to allow rigorous optimization within reasonable convergence time.

Later work focused on optimization of lean loading in the stripper (Alie et al., 2004) and stripper pressure (Freguia et al., 2003). Complex configurations with an objective of reducing the energy requirement of the stripping system were studied and optimized to make the technology more attractive. Some of these configurations modeled for MEA were Vapor Recompression, Multipressure Stripping and Multipressure with Vapor Recompression (Jassim et al., 2006) which showed promising performance. Other configurations were Matrix Stripper, Internal Exchange Stripper and Flashing Feed Stripper (Oyenekan et al., 2006). Full cost analysis of these configurations has also showed superiority of advanced configurations (Karimi et al., 2011). Some of the latest innovations in this field have been modifications like cold rich bypass and the interheated stripper (Van Wagener, 2011).

Process modeling and rigorous optimization of parameters like operating pressure and solvent circulation rate with respect to the entire system and its integration with the power plant has also been a topic of interest and studied using stripper modeling (Cifre et al., 2009).

While Aspen Plus® has been the choice of modeling software for most (Jassim et al., 2006) (Van Wagener, 2011); modeling has also been done in GAMS (General

Algebraic Modeling System) (Mores et al., 2011), Aspen Custom Modeler (Oyenekan et al., 2006), and CO2SIM (Kvamdsal et al., 2009).

Modeling of pilot scale experiments to validate the solvent models based on bench scale experiments has been well studied. These pilot scale experiments are important to demonstrate the technology on a bench scale and quantify the energy requirement. It is an important topic of research for companies (Sander et al., 1992). New solvents (MDEA and activated MEA) and flue gas composition representing natural gas have also been studied (Erga et al., 1995). Pilot plants were also built on actual flue gas conditions for demonstration and data was used for absorption and mass transfer modeling (Wilson et al., 2004). In recent years, complex configurations have been tested on pilot scale for new solvents like piperazine and have demonstrated the superiority of solvents and configurations (Chen et al., 2013).

Details of prior work results of individual stripper modeling are given in their respective chapter.

1.4 Research Objectives

This work accomplishes the following objectives:

1. Comparison of energy performance of complex stripper configurations for piperazine for CO_2 capture
2. Optimization of stripper configurations for best energy performance across operating range
3. Innovation and evaluation of new stripper configurations
4. Evaluation of solvent model performance for pilot campaigns of piperazine conducted under Carbon Capture Pilot Plant Project, University of Texas at Austin

5. Evaluation of energy performance for carbon capture application in post combustion flue gas from natural gas fired power plants

1.4.1 Scope of Work

This work builds upon some of the previous configurations that have been studied in the past by previous researchers. A consistent set of design specification are identified and utilized for process modeling for comparison of energy performance for multiple stripper configurations.

This work uses the latest available thermodynamic and kinetic model for piperazine-carbon dioxide-water to simulate complex stripper configurations. Optimization of various operating conditions is performed to identify best performance.

Innovation and quantification of new stripper configurations with an objective of minimum energy requirement is the prime objective of this research. The work evaluates and proposes a new stripper configuration which reduces the overall energy requirement of the process.

This work also includes data reconciliation of pilot plant campaigns using Aspen Plus® Data Fit to identify and quantify the error between measured and model value. This is important to validate the model and recommend necessary steps for improving pilot plant operations and model improvements.

Lastly, this work evaluates the implementation of amine scrubbing in natural gas fired power plant from energy requirement point of view. It uses various complex configurations to quantify the energy performance of carbon capture from natural gas fired power plants.

Chapter 2: Stripper Configurations

This chapter uses the concepts of complex stripper configurations to evaluate and identify the best stripper configuration with minimum energy requirement for amine scrubbing using piperazine. The conventional regeneration system uses a simple stripper but research has shown promising results for complex configurations (Van Wagener, 2011) (Oyenekan, Modeling of Strippers for CO2 Capture by Aqueous Amines, 2007). In this work, process design specifications are identified and various stripper configurations are evaluated, compared and optimized for these design specifications. The simulations in this Chapter were performed with the Fawkes model.

2.1 Stripper complexity

Energy requirement can be reduced in two ways. Solvents with desirable characteristics of high heat of absorption, high resistance to thermal degradation and high carbon dioxide carrying capacity are useful for better energy performance. Piperazine (PZ) is one such solvent with desirable properties and has demonstrated better energy performance in modeling and pilot scale experiments (Rochelle et al., 2011).

The other important aspect for reducing the energy requirement is stripper complexity which increases the associated reversibility of the process by reducing driving forces (Leites, 2003). In a conventional absorber/stripper configuration, work is lost in different ways. These are due to large driving force and associated irreversibility in cross-exchanger, evaporation of water along with CO_2, loss in compression work, etc. Calculation of theoretical work for 90% removal of CO_2 from coal fired power plant predicts a minimum possible work of 113 kWh/tonne (19 kJ/mol) (Rochelle et al., 2011) required for separation. This number assumes a final pressure of 150 bar for carbon dioxide. Modeling of the absorber/stripper configuration has generally predicted an energy requirement of about twice this number.

Adding complexity in the regeneration configuration reduces the overall energy requirement by improving the reversibility of the process. Such complexities typically involve separating CO_2 at multiple pressure and temperature levels, better heat recovery from the hot products, or reducing the stripping steam produced with the CO_2 (Van Wagener, 2011).

2.1.1 Equivalent Work

Energy performance of an amine scrubbing process is calculated as 'Total Equivalent Work' which represent the sum of equivalent work which the steam would have been produced if not used in the amine regeneration process and the total electricity requirement for compression and pumping in the process (Oyenekan, 2007). It is normalized to per mole of CO_2 produced in the process as given below.

$$W_{eq}\left(\frac{kJ}{mol\ CO_2}\right) = 0.75\left[\frac{T_{reb} + 5 - 313}{T_{reb} + 5}\right] Q_{reb} + W_{comp} + W_{pump}$$

Equation 1: Total Equivalent Work

First term in the equation calculates the equivalent work of the steam used in the reboiler using Carnot efficiency and reboiler duty (Q_{reb}). Power cycle efficiency of 0.75, approach temperature of 5 K and a sink temperature of 40°C are assumed for the calculations. The other two terms represent the work requirement in the compressors and pumps of the process.

For this work, pump work is taken from Aspen Plus® calculations and compressor work is calculated using the equation below (Van Wagener, 2011). This equation is regressed using compression work calculated in Aspen Plus® using a multistage compressor for 150 bar discharge pressure. Using this regressed equation helps in avoiding compression simulation for each operating case.

$$W_{comp}\left(\frac{kJ}{mol\ CO_2}\right) = \begin{cases} 4.572\ln\left(\frac{150}{P_{in}}\right) - 4.096 & P_{in} \leq 4.56\ bar \\ 4.023\ln\left(\frac{150}{P_{in}}\right) - 2.181 & P_{in} > 4.56\ bar \end{cases}$$

Equation 2: Work of compression, 72% efficiency, $P_i/P_{i-1} \leq 2$, intercooling to 40°C with no ΔP

Pump work calculations in Aspen Plus® assumed an efficiency of 72%.

2.1.2 Prior Work

Few research papers have been published with a focus on new stripper configurations. Table 1 summarizes the total equivalent work and important aspects of some of the complex configurations reported in the past.

Table 1: Equivalent Work calculated in prior work for various configurations

Stripper Configuration	**Solvent**	**Equivalent Work (for CO_2 compressed to 150 bar)**	**Comments**
Simple Stripper (Desideri et al., 1999)	MEA	39.0 kJ/mol	Estimated from 3.95 GJ/t heat duty and 47.6 kWh/t compressor

Simple Stripper with lean flash (Reddy et al., 2003)	Econamine[SM]	39.7 kJ/mol	Estimated from reported reboiler duty of 1395 BTU/lb and 0.55 bar-g pressure
Simple Stripper (Jassim et al., 2006)	MEA	42.8 kJ/mol	Estimated from reported 1.04 GJ/ton
Multipressure (Jassim et al., 2006)	MEA	39.0 kJ/mol	Estimated from reported 0.96 GJ/ton
Double Matrix (Oyenekan, Modeling of Strippers for CO2 Capture by Aqueous Amines, 2007)	K^+/PZ	32.5 kJ/mol	
Internal Exchange (Oyenekan, Modeling of Strippers for CO2 Capture by Aqueous Amines, 2007)	K^+/PZ	34.2 kJ/mol	
Simple Stripper (Mitsubishi, 2009)	KS-1[TM]	36.3 kJ/mol	
Split Stream (Karimi et al., 2011)	MEA	36.4 kJ/mol	
Vapor Recompression (Karimi et al., 2011)	MEA	36.9 kJ/mol	
Interheated Stripper (Van Wagener, 2011)	PZ	30.9 kJ/mol	
2-stage flash with bypass (Van Wagener, 2011)	PZ	30.7 kJ/mol	

2.2 COMPLEX STRIPPER CONFIGURATIONS

One of the issues with most of the previous work is the inconsistency among different design specifications used for modeling and simulation. This work improves upon some of the important configurations by analyzing and identifying a consistent set of design specifications that can be used across different stripper configurations. These design specifications are used for modeling and optimization of complex configurations to identify the best configuration for carbon capture using piperazine.

2.2.1 Process Design Specifications

Major design specifications required for simulation were analyzed in this study. Figure 3 shows the important design elements of a conventional stripping system. Table 2 highlights the inconsistencies across the previous work with respect to different process modeling specifications. For comparison of different stripper configurations, it is extremely important to have the same set of design specifications across the configurations.

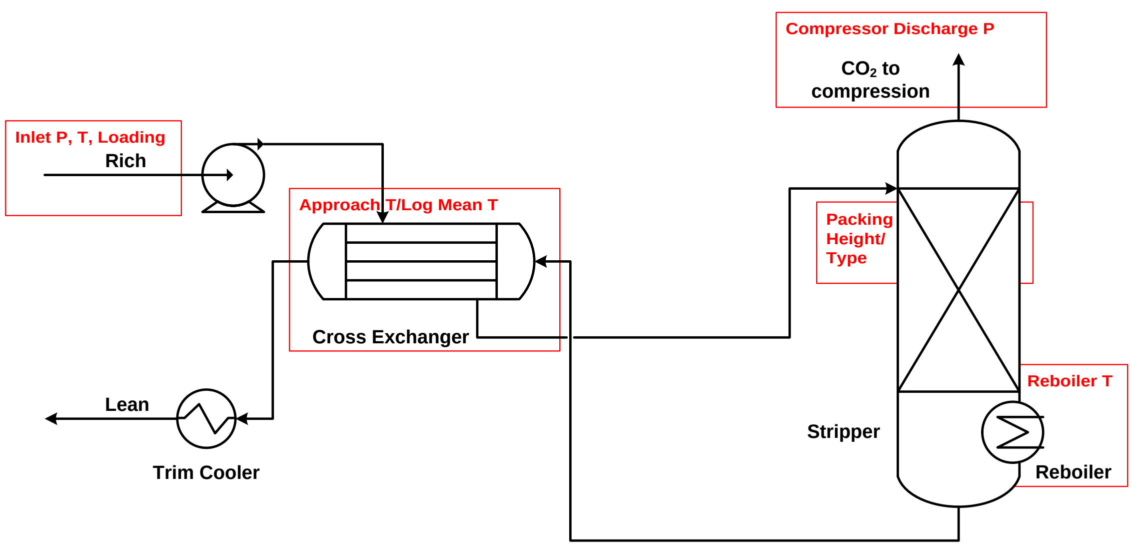

Figure 3: Main design elements of stripping section of amine scrubbing

Table 2: Design Specifications in major previous works on stripper configurations

	Solvent	Design Specifications
Jassim (2006)	MEA	5/10°C Hot Side Approach 123°C Stripper T Constant Stripper P
Oyenekan (2007)	MEA K^+/PZ Promoted MEA	5/10°C Hot Side Approach
Karimi (2011)	MEA	5/10°C Hot Side Approach
Van Wagener (2011)	MEA PZ	5°C Cold Side Approach/5 C LMTD 150 bar discharge P Compressor-work correlation 150°C stripper T (PZ) 120°C stripper T (MEA)

2.2.1.1 Modeling Parameters

A thermodynamic model of Piperazine-Carbon Dioxide-Water based on the e-NRTL framework was created in Aspen Plus®. Model parameters were regressed using experimental results and predicted values match well with the experimental results. The Fawkes model (Frailie et al., 2011) released in 2011 was used for these simulations.

Rate based mass transfer is the rigorous and preferred method used for stripper modeling (Aspen Plus® RadFrac) in Aspen Plus®. At the high temperature of the stripper, equilibrium reactions are expected and an equilibrium reaction model was used with rate based mass transfer. Figure 4 shows the set of speciation reactions used in the process model.

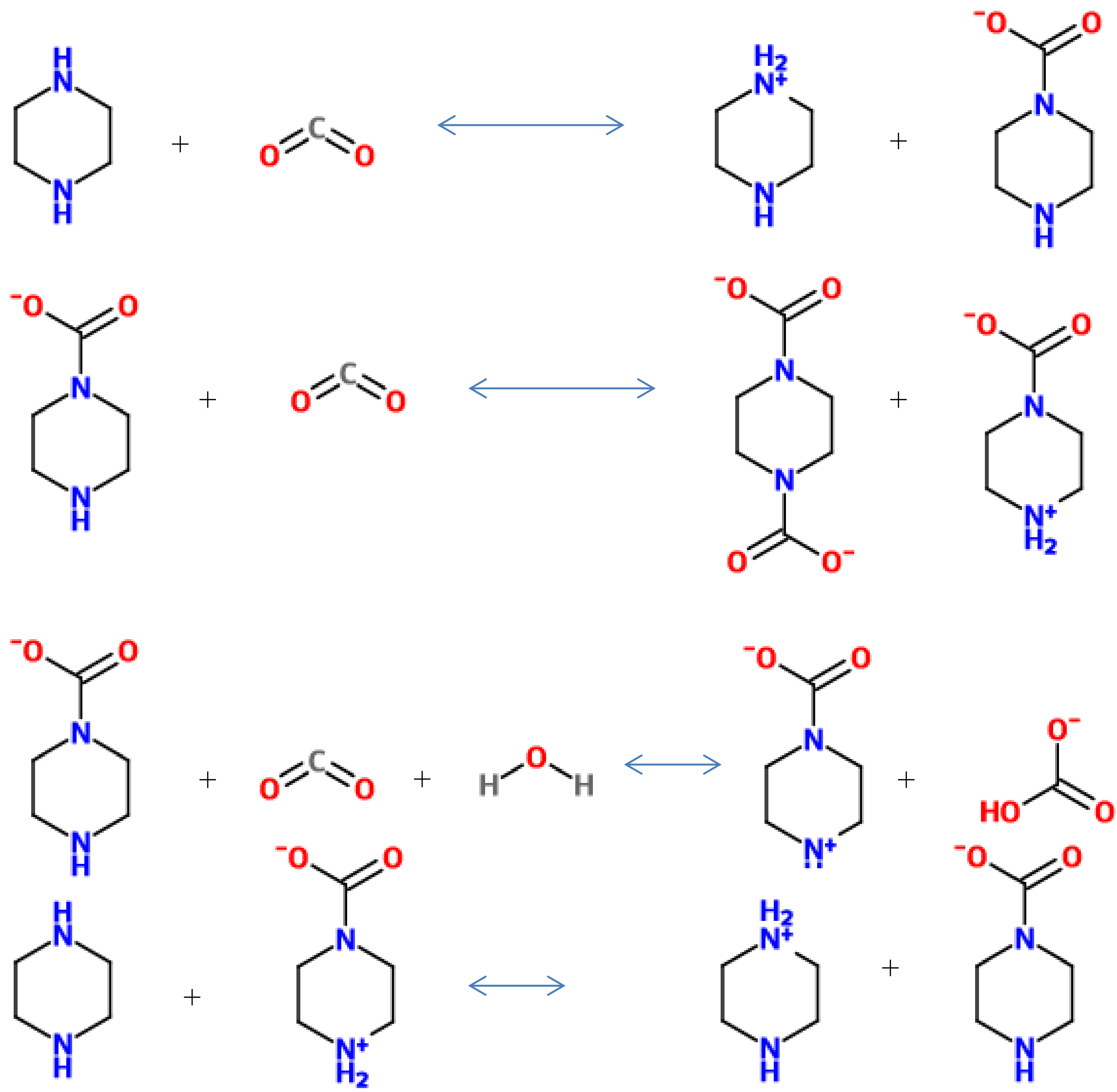

Figure 4: Piperazine speciation reactions

A solvent concentration of 8 molal (40 wt %) was used.

2.2.1.2 Stripper Temperature

Higher stripper temperature is expected to provide a better energy performance for the entire system due to an increased stripper pressure which decreases the compression requirement and to less stripping steam produced during the separation (Van

Wagener, 2011). However, the maximum temperature is determined by the thermal degradation limit of the solvent. The thermal degradation limit for 8m piperazine is estimated as 165°C (Freeman et al., Degradation of aqueous piperazine in carbon dioxice capture, 2010).

Also, high stripping temperature requires high temperature steam which is more valuable and hence can tend to increase the overall equivalent work. This is especially probable for a two pressure stage separation system which typically operates at a higher pressure than a simple stripper system.

Two stripper configurations were tested for a range of operating conditions of their stripping temperature to identify the optimum value of stripper temperature. These configurations are shown in Figure 5 and Figure 6 and represent the two of the best configurations identified in previous research work. These configurations of interheated stripper and two-stage flash with bypass are discussed later in the chapter.

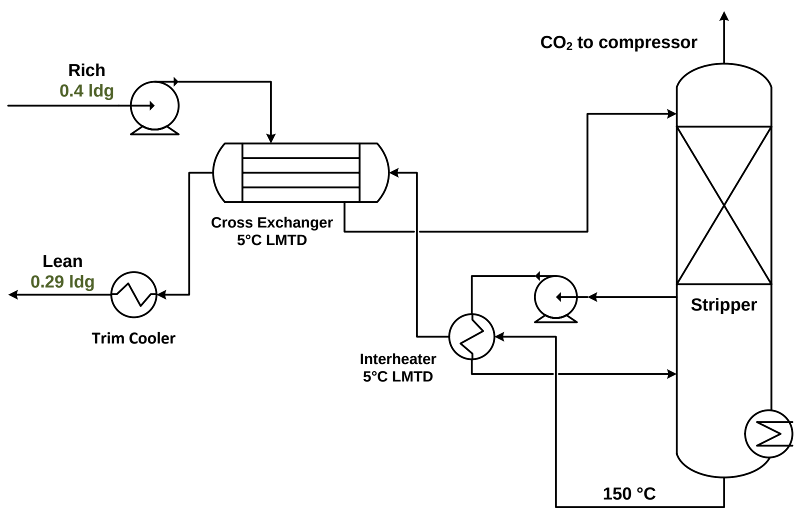

Figure 5: Interheated stripper configuration (Flashing cross exchangers)

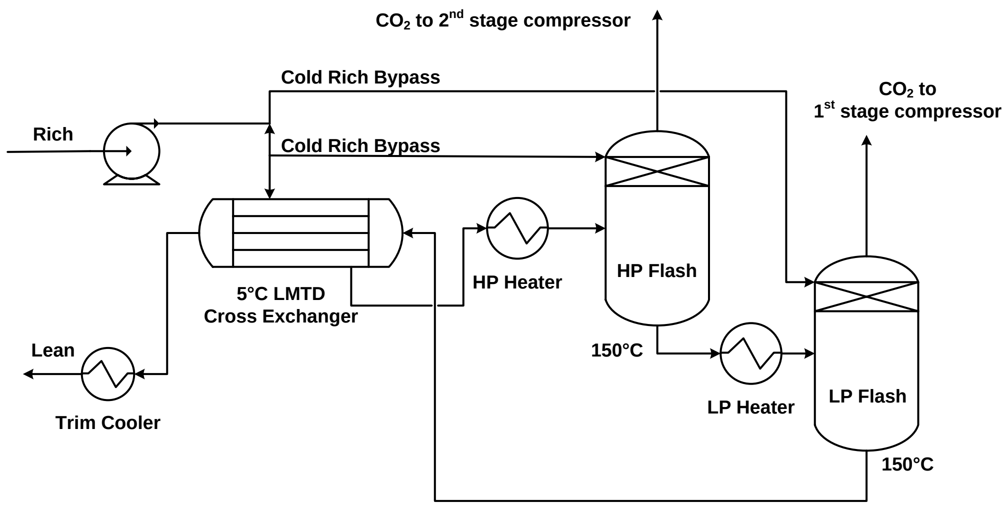

Figure 6: Two-stage flash with cold rich bypass (Non-flashing cross exchangers)

Figure 7 and Figure 8 shows the equivalent work values for the two configurations for stripper temperatures of 140°C, 150°C and 165°C and a range of lean loading.

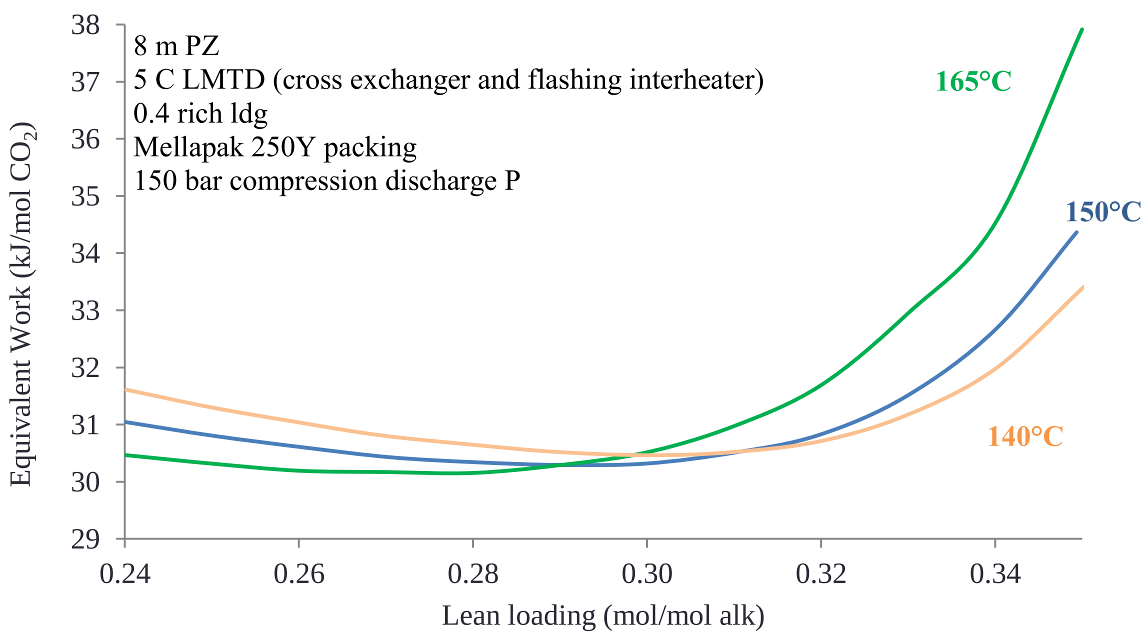

Figure 7: Equivalent work for interheated stripper (Variable lean loading, variable stripper temperature)

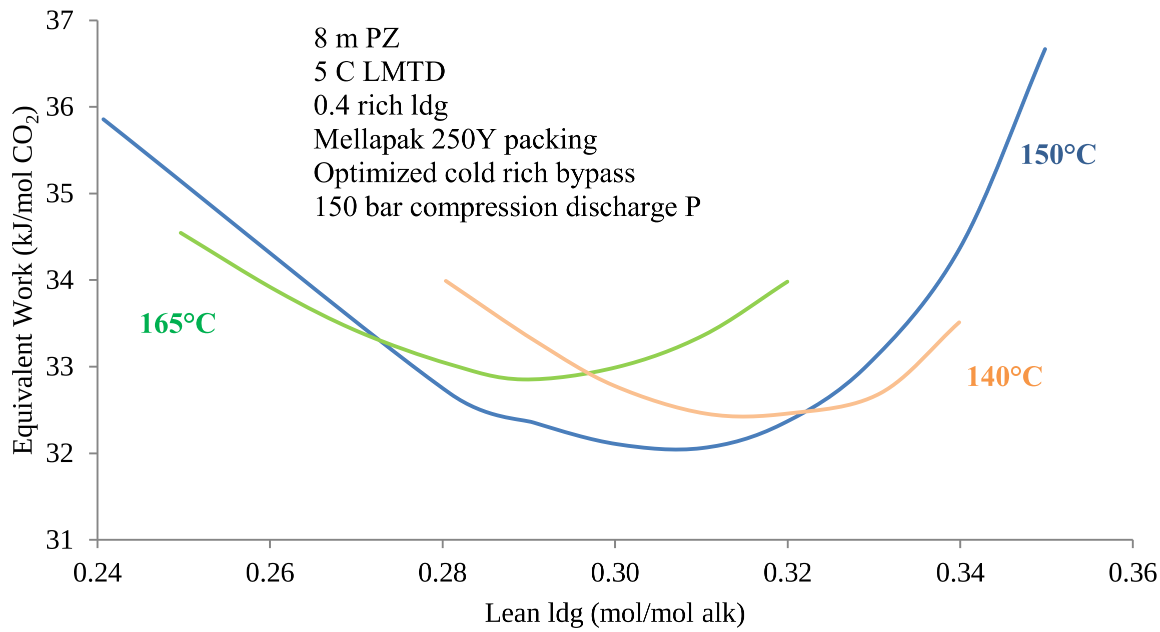

Figure 8: Equivalent work for 2-stage flash with cold rich bypass (Variable lean loading, variable stripper temperature, bypass flow optimized for each lean loading)

For the interheated stripper, increasing the temperature had an expected effect and the optimum value of equivalent work decreased with an increase in the stripper temperature. However, the benefit was small and less than 1% for every 10°C increase.

For the two-stage flash configuration, there was a noticeable decrease in equivalent work when temperature was changed from 140°C to 150°C; however, further increase in temperature resulted in an increase in equivalent work. This was mainly due to an increase in T_{reb} in reboiler equivalent work which implies that the high temperature steam required for high stripper T is more valuable. 150°C was found as an optimum temperature for this configuration.

Hence, a temperature of 150°C was selected for this specification.

2.2.1.3 Cross Exchanger Specification

Three different exchanger design specifications were analyzed, corresponding to 5°C hot side approach, 5°C cold side approach and 5°C LMTD. Table 3, Table 4 and Table 5 gives the calculated value of cross exchanger UA for different values of lean loading for each of the specifications.

Table 3: Cross exchanger design for a range of lean loading for 5°C hot side approach (8m PZ, single stage flash, 0.4 rich loading, 150°C heater)

Lean ldg	**Hot Side approach T**	**Cold Side approach T**	**LMTD**	**UA**
0.25	5.0	-4.0	0.0	*
0.26	5.0	-2.4	0.0	*
0.27	5.0	-1.1	0.0	*
0.28	5.0	0.1	1.1	433.3
0.29	5.0	1.0	2.5	190.5
0.30	5.0	1.9	3.2	149.1
0.31	5.0	2.7	3.7	129.5
0.32	5.0	3.2	4.1	118.4
0.33	5.0	3.8	4.4	110.2
0.34	5.0	4.3	4.6	103.7

With a 5°C hot side approach (Table 3), the cross exchanger had a practical design for high lean loading but had impractically high heat transfer area for low lean loading. Hence, for simulating the entire range of lean loading, this is not a good choice.

Table 4: Cross exchanger design for a range of lean loading for 5°C cold side approach (8m PZ, single stage flash, 0.4 rich loading, 150°C heater)

Lean ldg	**Hot Side approach T**	**Cold Side approach T**	**LMTD**	**UA**
0.25	12.7	5.0	8.3	53.5
0.26	11.4	5.0	7.8	57.6
0.27	10.4	5.0	7.4	61.7
0.28	9.4	5.0	7.0	65.7
0.29	8.5	5.0	6.6	70.0
0.30	7.8	5.0	6.3	74.0
0.31	7.2	5.0	6.0	78.1
0.32	6.6	5.0	5.8	81.8
0.33	6.1	5.0	5.5	85.7
0.34	5.7	5.0	5.4	88.9

This specification of constant cold side approach T gave practical values for the entire range but the UA value tends to become more conservative for low lean loading. Using this specification will lead to conservative values of equivalent work, especially for lower lean loading.

Table 5: Cross exchanger design for a range of lean loading for 5°C LMTD design specification (8m PZ, single stage flash, 0.4 rich loading, 150°C heater temperature)

Lean ldg	**Hot Side approach T**	**Cold Side approach T**	**LMTD**	**UA**
0.25	10.1	2.0	5.0	90.9
0.26	9.1	2.4	5.0	92.0
0.27	8.3	2.7	5.0	92.8
0.28	7.6	3.0	5.0	93.5
0.29	7.1	3.4	5.0	94.0
0.30	6.6	3.7	5.0	94.4

0.31	6.2	3.9	5.0	94.9
0.32	5.9	4.2	5.0	95.1
0.33	5.6	4.5	5.0	95.4
0.34	5.4	4.6	5.0	95.7

This specification had a consistent value of UA for the entire range of lean loading and hence was the selected design specification for the work.

2.2.1.4 Other Specifications

The rich loading was held constant at 0.4 mol/mol alkalinity corresponding to a CO_2 partial pressure of 5 kPa at 40°C in the flue gas. Solvent molality at the rich feed was kept constant at 8 m.

The Inlet rich stream was simulated at 1 atm and 46°C. All results were normalized to per mole of CO_2 captured. A constant pressure drop of 1 bar was assumed for each operating case between the rich inlet and the stripper/flash separator.

Mellapak 250Y was used as packing material wherever required.

2.2.2 Process Optimization

2.2.2.1 Lean loading optimization

The Stripping system can be operated at a range of lean loading. A low value of lean loading results in better carbon dioxide carrying capacity but also leads to large amount of water vapor due to a decrease in the partial pressure of CO_2 in the product stream. There is also a decline in the total pressure which also leads to higher compression work (Van Wagener, 2011).

Thus, there is a trade-off leading to an optimum value of lean loading for each configuration for which total equivalent work is at its minimum. Each of the configurations studied in this process was optimized for lean loading.

2.2.2.2 Rich Bypass flow optimization

A high rich bypass for heat recovery leads to less water vapor in the product stream; however, if excess cold solvent is contacted with CO_2, there is also an enrichment of the cold solvent which has to be stripped further to achieve desirable lean loading. Hence, there is a trade-off in the bypass flow and the amount of flow has to be optimized for each configuration. Each of the configurations studied that included rich bypass flow was optimized for rich bypass flow.

Complex stripper configurations were divided into two categories, representing reboiler based stripper configurations and heater based flash configurations.

2.2.3 Reboiler based configurations

2.2.3.1 Simple Stripper

This is the base configuration among reboiler based configurations consisting of a simple packed column and reboiler system for heating and separating CO_2 from the solvent. The cold water from the stripper condenser is not returned to the stripper system.

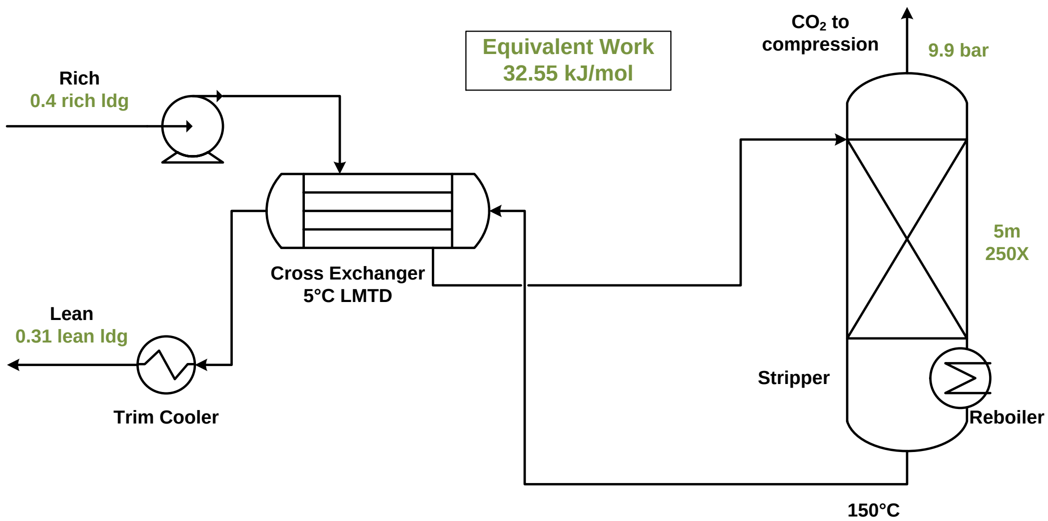

Figure 9: Simple Stripper Configuration (8m PZ, with optimum conditions of other operating variables)

The configuration was optimized for equivalent work by varying the lean loading. Table 6 gives the calculated value of equivalent work normalized per mole of CO_2 captured for the range of lean loading. Rich pump work calculated in Aspen Plus® using 75% efficiency pumps were used in this work. No work was assumed on the lean side.

Table 6: Equivalent Work for simple stripper (Variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C cross exchanger LMTD, 2 m M250Y)

Lean loading	**Cold side Approach T**	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Total Equivalent Work**
mol/mol alk	°C	kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.24	2.8	114.3	23.03	10.55	34.16
0.28	3.6	110.9	22.35	9.66	32.98
0.29	3.8	110.5	22.26	9.38	32.77

0.30	4.0	110.1	22.18	9.07	32.60
0.31	**4.2**	**110.1**	**22.19**	**8.75**	**32.55**
0.32	4.4	110.8	22.33	8.39	32.71
0.33	4.6	112.0	22.56	8.00	33.07
0.34	4.7	115.2	23.20	7.56	34.08
0.35	4.9	119.8	24.13	7.15	35.66

The optimum value of equivalent work for the simple stripper, 32.55 kJ/mol is similar to some values reported in previous work (Van Wagener, 2011).

2.2.3.2 Multipressure Stripper

The stripper in this configuration operates at two different pressure levels with a pressure ratio of 1.5. The vapor from the lower pressure bottom part of the stripper is re-injected to the bottom of the top half. This configuration has shown improvement over conventional designs in the past (Jassim et al., 2006).

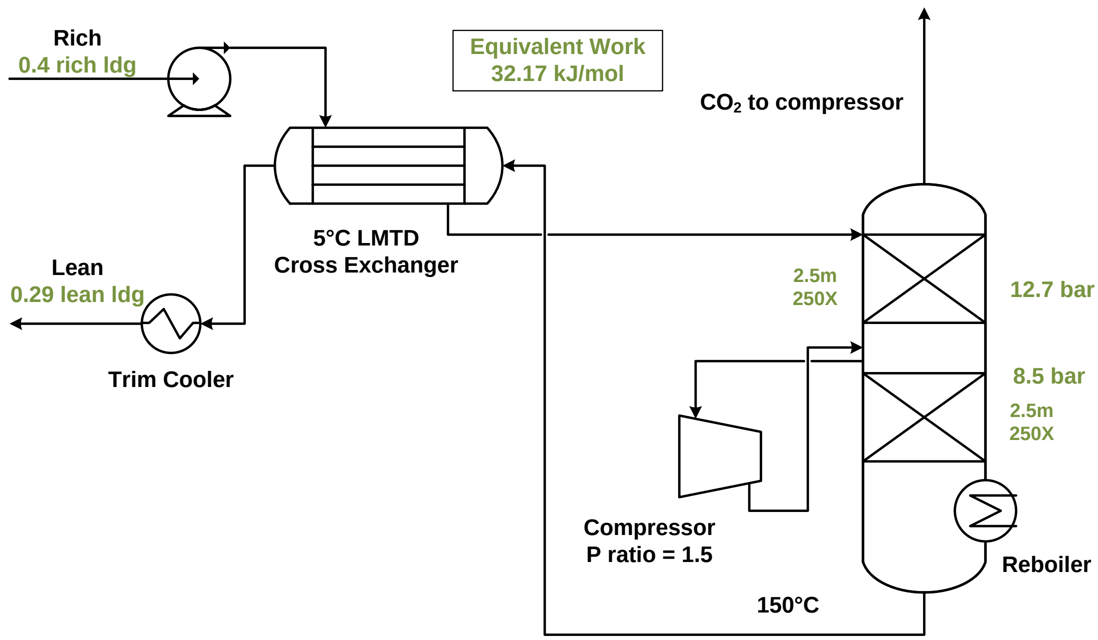

Figure 10: Multipressure stripper configuration (8m PZ, non-flashing cross exchanger, with optimum conditions of other operating variables)

Table 7 gives the calculated value of equivalent work normalized per mole of CO_2 captured for the range of lean loading.

Table 7: Equivalent Work for multipressure configuration (Variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C cross exchanger LMTD, 5m Mellapak 250Y)

Lean loading	**Cold Side Approach T**	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Total Equivalent Work**
mol/mol alk		kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.25	3.0	102.6	20.67	10.95	32.92
0.26	3.2	102.1	20.58	10.75	32.67
0.27	3.4	101.7	20.48	10.52	32.44

0.28	3.6	101.4	20.43	10.26	32.27
0.29	3.8	101.2	20.39	9.99	32.17
0.30	4.0	**101.3**	**20.41**	**9.69**	**32.17**
0.31	**4.2**	101.7	20.48	9.36	32.32
0.32	4.4	102.6	20.68	9.00	32.73
0.33	4.6	104.4	21.02	8.62	33.50
0.34	4.7	107.5	21.65	8.22	34.90

2.2.3.3 Simple Stripper with cold rich bypass

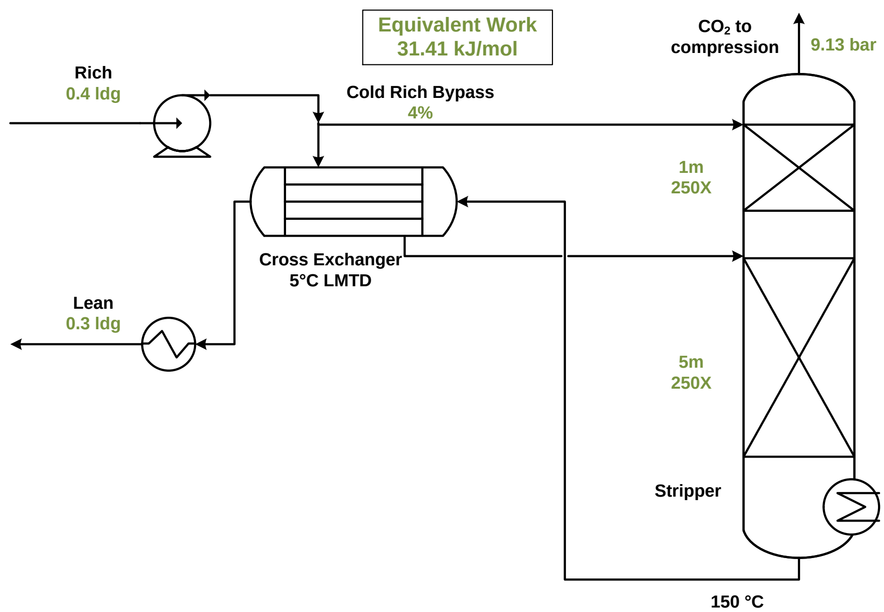

Figure 11: Simple Stripper with cold rich bypass configuration (8m PZ, non-flashing cross exchanger, optimum operating conditions shown)

This concept of cold rich bypass for heat recovery from stripping steam in the CO_2 product has shown promising results in the past (Van Wagener, 2011). This configuration was simulated with the new set of design specifications with 8 m PZ solvent. In this configuration, a small amount of cold solvent is used to recover the heat lost with the water vapor in the CO_2 product stream.

Table 8 gives the calculated value of equivalent work normalized per mole of CO_2 captured for the range of lean loading.

Table 8: Equivalent Work for simple stripper with cold rich bypass (Variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C cross exchanger LMTD)

Lean loading	**Cold Side Approach T**	**Bypass Fraction**	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Total Equivalent Work**
mol/mol alk	°C		kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.24	8.9	10%	108.9	21.94	10.51	33.04
0.28	7.1	6%	104.9	21.13	9.65	31.75
0.29	6.7	5%	104.5	21.05	9.37	31.55
0.30	6.4	**4%**	**104.3**	**21.00**	**9.08**	**31.41**
0.31	5.9	3%	104.7	21.09	8.73	31.45
0.32	5.9	3%	105.4	21.24	8.40	31.61
0.33	5.7	2%	107.4	21.64	7.97	32.16
0.34	5.4	2%	110.1	22.18	7.61	33.00
0.35	4.9	1%	115.4	23.25	7.18	34.73

2.2.3.4 Interheated Stripper

This configuration has shown best results among all complex configurations in the past. It consists of two stage heat recovery from the lean solvent using an interheater as shown in Figure 12. The Pump work for the interheater is not included in the total equivalent work.

Table 9 gives the calculated value of equivalent work normalized per mole of CO_2 captured for the range of lean loading.

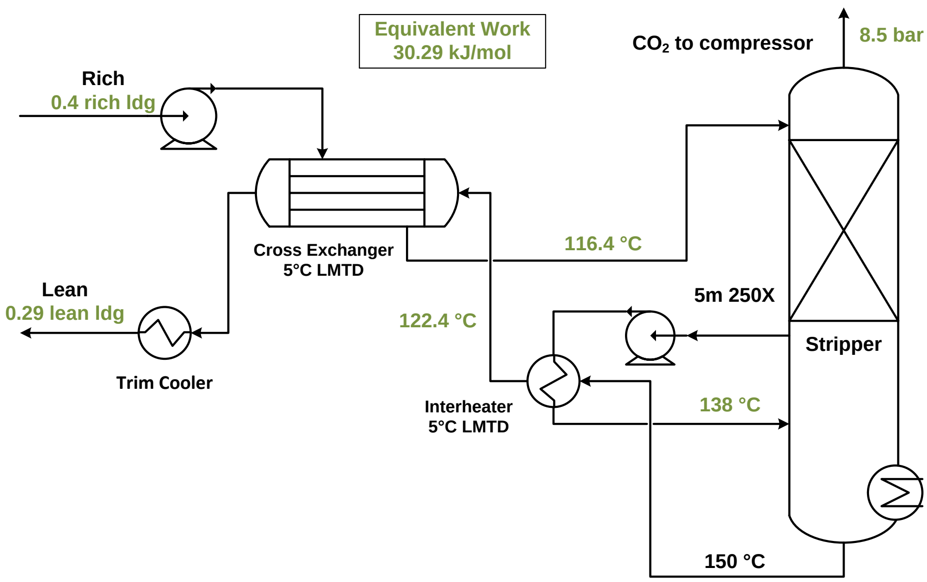

Figure 12: Interheated Stripper (8m PZ, non-flashing cross exchanger, optimum operating conditions shown)

Table 9: Equivalent Work for interheated stripper (Variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C cross exchanger LMTD)

Lean loading	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Total Equivalent Work**
mol/mol alk	kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.24	99.0	19.94	10.51	31.05
0.25	98.4	19.82	10.33	30.81
0.26	98.0	19.75	10.12	30.61
0.27	97.8	19.70	9.88	30.43

0.28	97.9	19.73	9.63	30.34
0.29	**98.3**	**19.79**	**9.36**	**30.29**
0.30	98.8	19.91	9.06	30.32
0.31	100.0	20.15	8.73	30.51
0.32	101.5	20.44	8.39	30.82
0.33	104.2	20.99	8.01	31.50
0.34	108.3	21.82	7.60	32.66
0.35	113.8	22.93	7.20	34.37

2.2.4 Heater based configurations

This category of configurations uses equilibrium flash (single or two stage), and a convective heater instead of conventional reboiler. Due to relatively simpler nature of these configurations, energy performance if these configurations are not expected to be as good as complex reboiler based configurations; however, these configurations have shown comparable performance and could be favored in certain commercial designs due to their simpler operation.

2.2.4.1 Single Stage Flash with cold rich bypass

This is an added complexity over the single stage flash by utilizing heat recovery with cold rich bypass. A small amount (1 to 2 m) of packing material is required to provide the contact area between the solvent and the water vapor rich product. This is the base case for heater based configurations in this work.

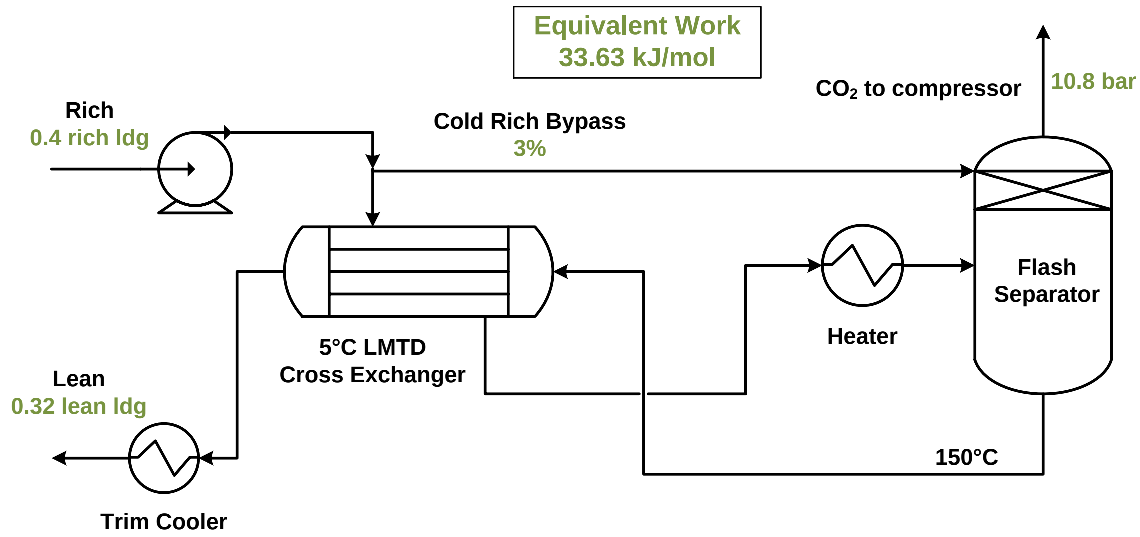

Figure 13: Single Stage Flash with cold rich bypass (8m PZ non-flashing cross exchanger, optimum conditions shown)

Table 10 gives the calculated value of equivalent work normalized per mole of CO_2 captured for the range of lean loading.

Table 10: Equivalent Work for a range of lean loading for single stage flash with cold rich bypass (8m PZ, 0.4 rich loading, 150°C stripper T, 5°C cross exchanger LMTD)

Lean loading	**Cold Side Approach T**	**Bypass fraction**	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Total Equivalent Work**
mol/mol alk			kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.24	10.4	14%	149.9	30.20	10.59	42.48
0.28	7.3	7%	124.4	25.06	9.66	36.24
0.29	7.0	6%	120.4	24.26	9.38	35.23
0.30	6.7	5%	117.4	23.65	9.09	34.46
0.31	6.3	4%	115.2	23.21	8.77	33.94

0.32	6.0	**3%**	**114.2**	**23.00**	**8.40**	**33.63**
0.33	6.3	3%	113.9	22.95	8.03	33.68
0.34	5.9	2%	117.6	23.69	7.57	34.70
0.35	6.0	2%	121.2	24.42	7.21	36.09

2.2.4.2 Two stage Flash

Separation is done at two different pressure levels in this configuration. This has an added advantage of reduced compression work since some of the CO_2 is produced at an elevated pressure. More than 2 pressure levels have been shown to provide diminishing return on energy requirement (Van Wagener, 2011).

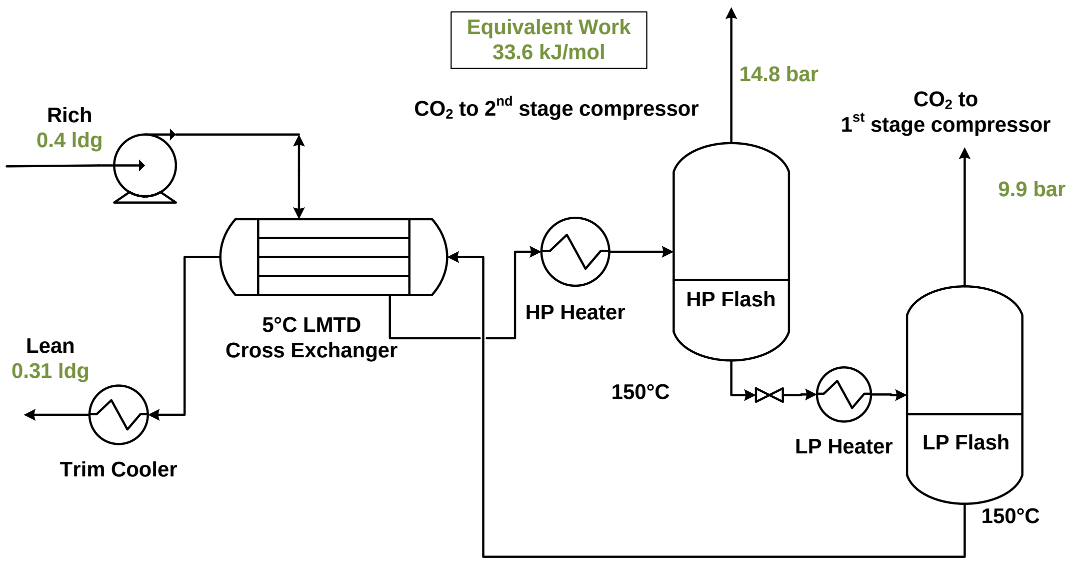

Figure 14: Two stage flash configuration (8m PZ, non-flashing cross exchanger, optimum operation conditions shown)

Table 11 gives the calculated value of equivalent work normalized per mole of CO_2 captured for the range of lean loading.

Table 11: Equivalent Work two stage flash (Variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C cross exchanger LMTD)

Lean loading	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Pump Work**	**Total Equivalent Work**
mol/mol alk	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2
0.24	143.29	29.30	9.61	0.87	39.78
0.28	123.50	25.11	8.74	1.42	35.27
0.29	120.08	24.39	8.47	1.67	34.53
0.30	117.41	23.82	8.18	1.99	33.99
0.31	**115.51**	**23.41**	**7.86**	**2.44**	**33.71**
0.32	114.68	23.22	7.56	2.99	33.77
0.33	115.07	23.28	7.22	3.83	34.33
0.34	116.50	23.56	6.95	4.81	35.32
0.35	120.06	24.26	6.67	6.34	37.27

2.2.4.3 Two stage Flash with cold rich bypass

This configuration has an added complexity of cold rich bypass on two stage flash separation for heat recovery.

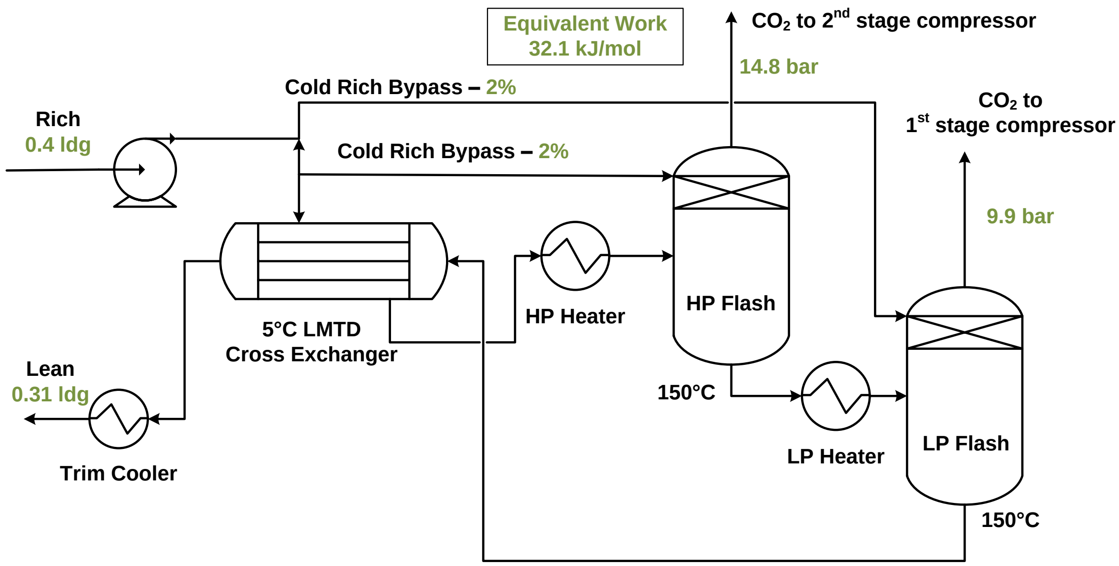

Figure 15: Two stage flash with cold rich bypass configuration (8m PZ, -non-flashing cross exchanger, 1m Mellapak 250X packing, optimum operation conditions shown)

Table 12 gives the calculated value of equivalent work normalized per mole of CO_2 captured for the range of lean loading.

Table 12: Equivalent Work for two stage flash with cold rich bypass (Variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C cross exchanger LMTD) add pump work, bypass rates

Lean loading	**Bypass Rate**	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Pump Work**	**Total Equivalent Work**
mol/mol alk		kJ/mol	kJ/mol	kJ/mol		kJ/mol
0.24	4%, 6%	124.6	25.10	9.61	1.15	35.86
0.28	3%, 3%	111.2	22.41	8.70	1.57	32.69
0.29	3%, 3%	109.7	22.09	8.44	1.82	32.35

0.30	2%, 2%	108.6	21.87	8.16	2.07	32.10
0.31	**2%, 2%**	**107.8**	**21.71**	**7.87**	**2.48**	**32.06**
0.32	1%, 2%	108.2	21.79	7.59	2.96	32.34
0.33	1%, 1%	109.6	22.08	7.28	3.65	33.01
0.34	1%, 1%	112.3	22.62	6.94	4.8	34.36
0.35	0.5%, 1%	117.4	23.66	6.65	6.36	36.67

2.2.4.4 Two stage Flash with low P/T flash

This is a two stage flash configuration with first stage operating at a low temperature and pressure than second stage. The lower temperature flash also helps in removing oxygen from the solvent system before it can enter high temperature stripping and cause oxidative degradation. For this simulation, LP flash was kept constant at 1 atm pressure and temperature was varied for optimum equivalent work.

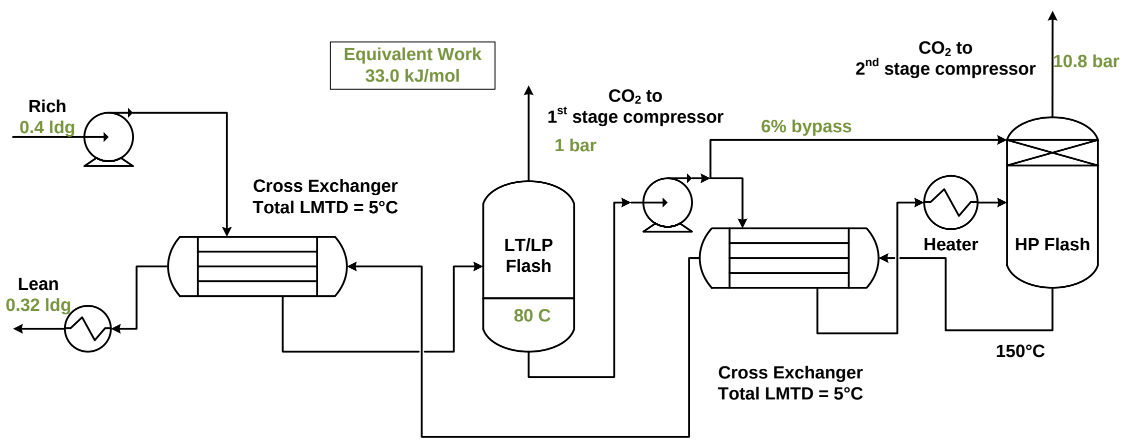

Figure 16: Two stage Flash with low P/T flash (8m PZ, 1 m Mellapak 250X packing, Low Pressure flash at 1 atm, optimized T of LP flash, non-flashing cross exchangers)

Table 13 gives the calculated value of equivalent work normalized per mole of CO_2 captured for the range of lean loading.

Table 13: Equivalent Work for two stage flash with low P/T flash (Variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C cross exchanger LMTD)

Lean loading	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Total Equivalent Work**
mol/mol alk	kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.24	123.9	24.96	12.41	39.04
0.28	112.0	22.56	10.89	34.88
0.29	108.5	21.85	10.77	34.12
0.30	105.9	21.33	10.63	33.52
0.31	109.4	22.05	9.39	33.15
0.32	**108.3**	**21.82**	**9.15**	**32.98**
0.33	108.3	21.82	8.92	33.07
0.34	113.3	22.83	7.94	33.71
0.35	113.2	22.81	8.53	35.06

Bypass flow at each loading was optimized for total equivalent work. Figure 17 compared the equivalent work for each value of lean loading.

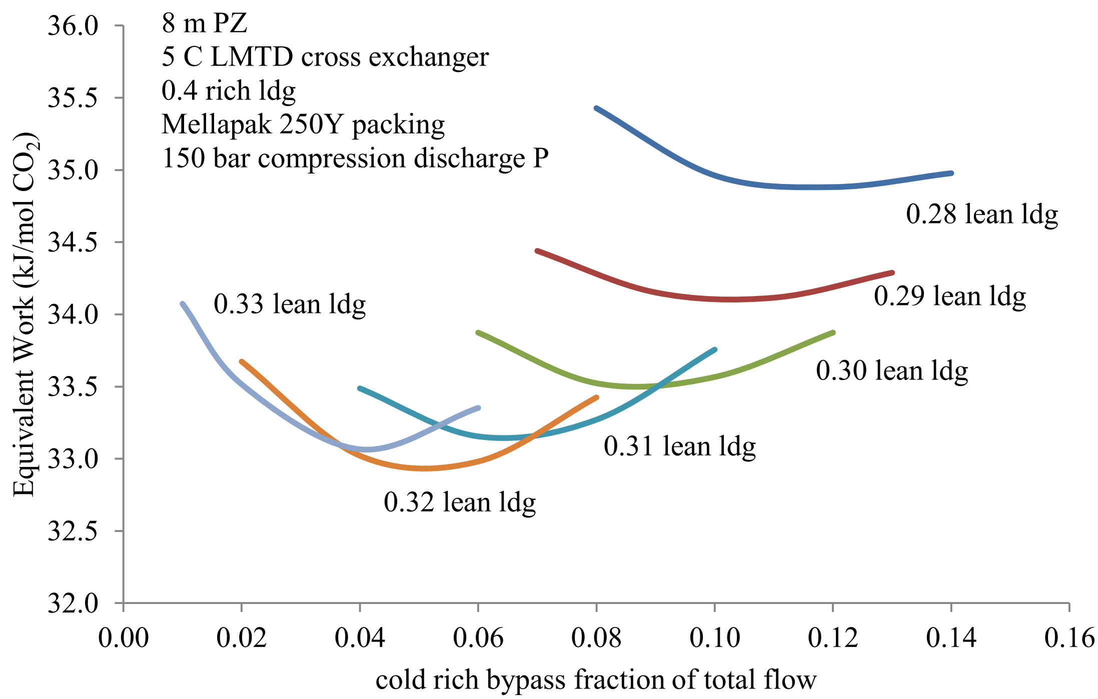

Figure 17: Equivalent Work for different lean loading for a range of cold rich bypass flow fraction for two stage flash with LP/LT flash configuration

2.2.4.5 Two stage interheated flash

This configuration operates at 2 temperature and 1 pressure levels. It is similar to interheated stripper system where the packed section is replaced by a single equilibrium flash.

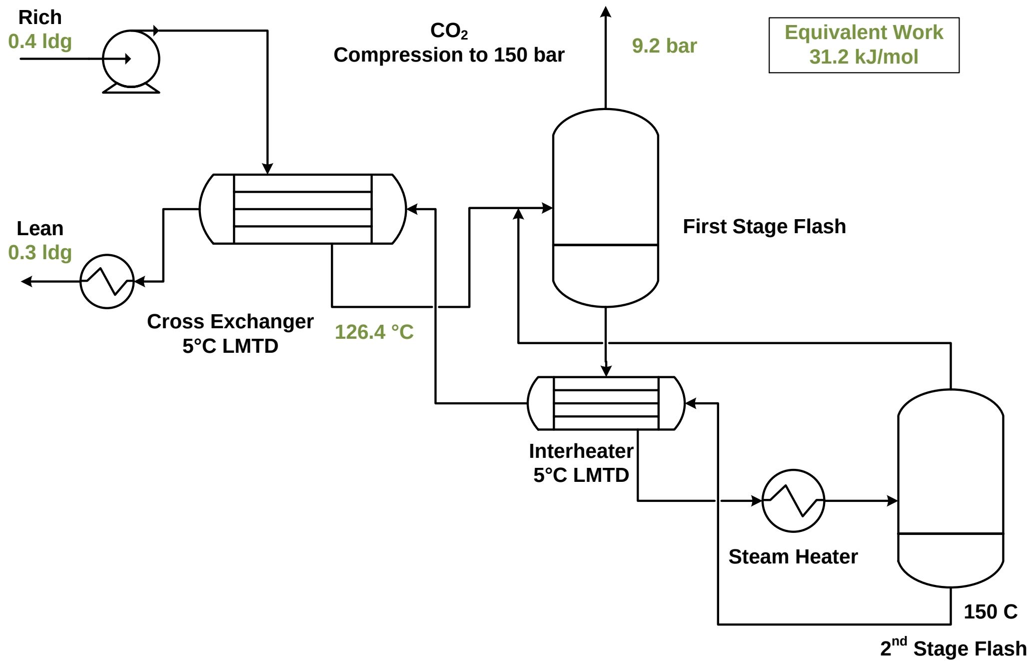

Figure 18: Two stage interheated flash (8m PZ, flashing exchanger, optimum conditions shown). For this configuration, a pump will probably be required for liquid discharge from first stage to second stage for proper pressure differential between the two stages.

Table 14 gives the calculated value of equivalent work normalized per mole of CO_2 captured for the range of lean loading.

Table 14: Equivalent work for interheated flash (Variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C cross exchanger LMTD)

Lean loading	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Total Equivalent Work**
mol/mol alk	kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.25	109.0	21.96	10.33	33.00

0.26	107.0	21.56	10.14	32.49
0.27	105.4	21.24	9.90	32.03
0.28	104.2	20.99	9.64	31.66
0.29	103.4	20.84	9.37	31.40
0.30	**103.0**	**20.75**	**9.05**	**31.22**
0.31	103.7	20.88	8.71	31.30
0.32	104.8	21.11	8.37	31.55
0.33	106.7	21.50	8.03	32.05
0.34	110.1	22.18	7.63	33.03

2.2.5 Comparison of Stripper Configurations

The optimum values for each configuration are compared against each other in Table 15. The best among heater based configurations was two stage flash interheating which had an improvement of 7.5% over the base case of single stage flash with cold rich bypass.

Among reboiler based configurations, interheated stripper had the best performance with 29.9 kJ/mol equivalent work, which is 8% better than the base case of simple stripper.

Table 15: Equivalent Work for all configurations at their optimum operating condition (8m PZ, 5°C LMTD cross exchanger, compression to 150 bar, Fawkes model)

Configuration		**Equivalent Work (kJ/mol CO_2)**	**Improvement over base case**
1-SF with bypass[1]	114.2	33.7	-
2-SF	115.5	33.7	0%
2-SF with LP/LT flash[2]	108.3	33.0	2%
2-SF with bypasses[3]	107.8	32.1	5%
2-SF interheating	**103.0**	**31.2**	**7.5%**
Simple Stripper	110.1	32.6	-
Multipressure	101.3	32.1	1.5%
SS with cold rich bypass[4]	104.3	31.4	4%
Interheated stripper	**98.3**	**29.9**	**8%**

Figure 19 compares the value of equivalent work across the range of lean loading for different heater based configurations.

Figure 20 compares the value of equivalent work across the range of lean loading for different reboiler based configurations

[1] Optimum bypass flow of 3% and 0.32 lean ldg
[2] Optimum bypass flow of 6% and 0.32 lean ldg
[3] Optimum bypass flow of 2% and 2% and 0.31 lean ldg
[4] Optimum cold rich bypass flow of 4% and 0.30 lean ldg

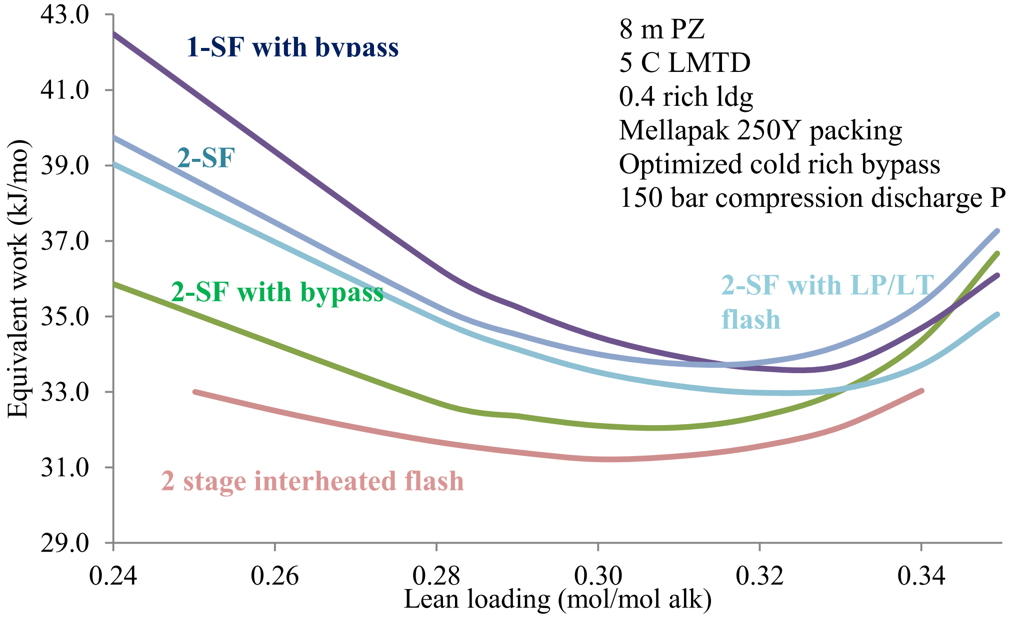

Figure 19: Equivalent Work for different heater based configurations (Variable lean loading, optimized cold rich bypass, Fawkes model)

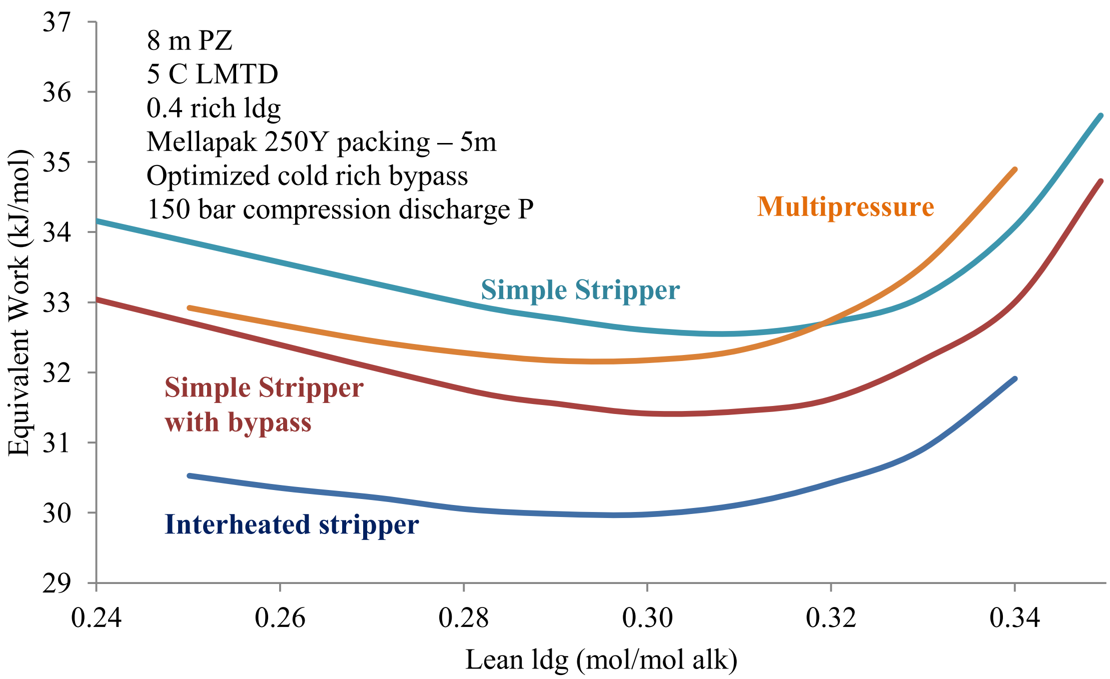

Figure 20: Equivalent Work for different reboiler based stripper configurations (Variable lean loading, optimized cold rich bypass, Fawkes model)

2.3 CONCLUSIONS

1. Modeling and simulation of MEA based capture plants have shown equivalent work values in range of 34 to 39 kJ/mol CO_2.
2. Complex configurations have shown performance improvement for both MEA and piperazine based configurations.
3. Design specifications of 5°C LMTD for cross exchanger and 150°C stripper temperature were selected for simulation of different configurations with 8m PZ.
4. Base cases of single stage flash with bypass and simple stripper had equivalent work values of 33.7 and 32.6 kJ/mol respectively. These were found to be consistent with available literature.
5. Two stage interheated flash has the best performance among heater based configurations with 31.2 kJ/mol equivalent work.
6. Interheated stripper has the best performance among stripper based configurations with 29.9 kJ/mol equivalent work.

Chapter 3: Advanced Flash Stripper

This chapter introduces a new concept of the advanced flash stripper which is an innovative configuration utilizing advanced heat recovery and reversible separation. This configuration uses a combination of flash separation and stripping separation by gas-liquid contact for lean solvent regeneration from rich solvent.

3.1 INTRODUCTION

Chapter 2 introduced various complex stripper configurations built upon the ideas of heat recovery and reversible separation which have shown better energy performance than conventional strippers (Van Wagener, 2011). The Advanced Flash Stripper uses a combination of reversible heat recovery at multiple temperature levels using combinations of solvent bypass at different temperature levels.

3.2 STRIPPER MODELING

3.2.1 Modeling Parameters

The Independence model for MDEA/PZ was available for this work and was used for modeling the configurations in Aspen Plus®. The Independence model incorporates a much larger set of experimental data than Fawkes used previously for analysis of other configurations, including data on low temperature CO_2 solubility, speciation for MDEA/PZ and amine volatility in loaded solution (Frailie et al., 2012).

Other modeling parameters were the same as used in the previous chapter for analysis of other configurations i.e. equilibrium based reaction and rate based mass transfer in regeneration system.

The following process parameters were kept constant in all simulations.

1. Rich loading – 0.4 mol/mol alk
2. Inlet solvent conditions – 1 atm and 46°C

3. Cross exchanger – 5°C LMTD non-flashing
4. Flash Stripper – Packing of Mellapak 250X and main feed onstage

Lean loading and bypass flow were optimized for all simulations.

3.2.1.1 Comparison of Fawkes and Independence Model

The simple stripper configuration was simulated with both the Fawkes and Independence models to quantify the difference of equivalent work values calculated using the two models. All the other parameters were kept exactly the same for the two models i.e. 0.4 rich loading, LMTD of 5°C in the cross exchanger, and 150°C reboiler temperature.

Table 16 shows the values of equivalent work for various values of lean loading for simple stripper using the Independence model.

Table 16: Equivalent work for simple stripper (Independence model, variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C non-flashing cross exchanger LMTD)

Lean loading	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Total Equivalent Work**
mol/mol alk	kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.28	106.8	21.5	9.94	32.37
0.30	**106.1**	**21.4**	**9.32**	**31.98**
0.32	107.0	21.6	8.69	32.09
0.34	112.5	22.7	7.84	33.62

Figure 21 and Table 17 shows the comparison of Equivalent Work values for the simple stripper configuration with the two solvent models.

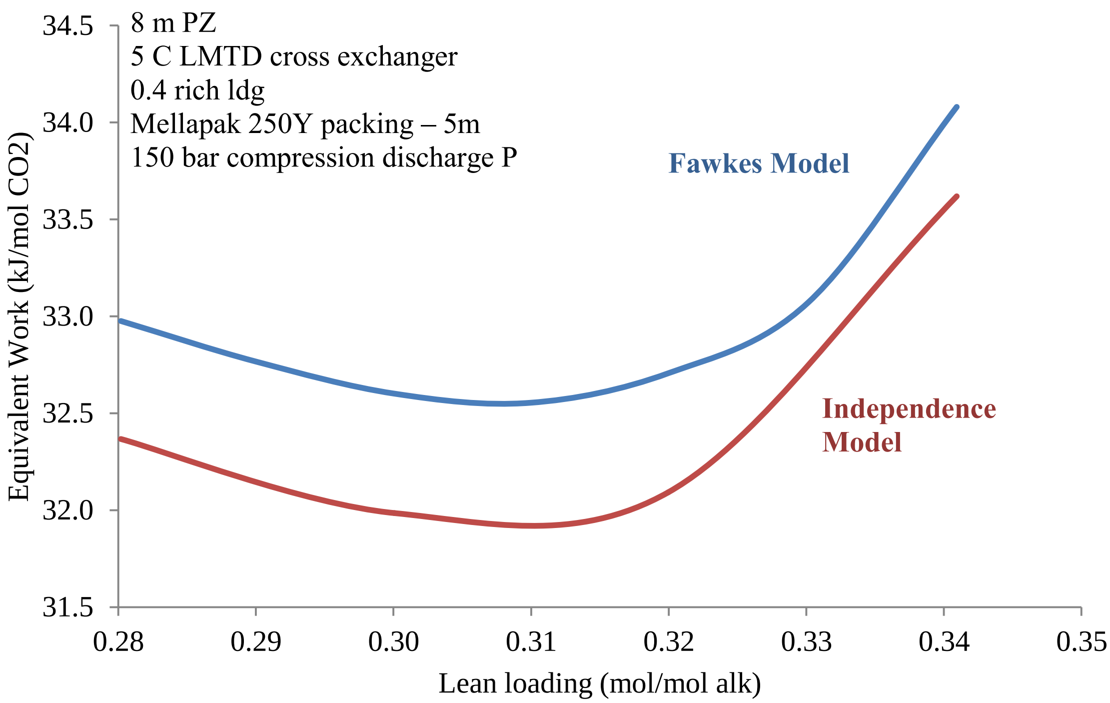

Figure 21: Equivalent Work comparison for simple stripper configuration using Fawkes and Independence models (Variable lean loading)

Table 17: Equivalent work comparison between Fawkes and Independence model for simple stripper (8m PZ, 5°C LMTD cross exchanger, 150°C reboiler T)

Lean loading	Equivalent work (Fawkes)	Equivalent Work (Independence)	Deviation of Fawkes model
mol/mol alk	kJ/mol CO_2	kJ/mol CO_2	%
0.28	32.98	32.37	1.9
0.30	32.60	31.98	1.9
0.32	32.71	32.09	1.9
0.34	34.08	33.62	1.4

Multiple complex levels of advanced flash stripper were simulated with the following process modeling parameters.

3.2.2 Process Modeling Parameters

Three major complexity levels studied were as follows

1. Advanced Flash Stripper 1 – This is the basic configuration with minimal complexity and is an optimized version of cold rich bypass. In this configuration, rich solvent bypass is taken at an optimum temperature by using two cross exchangers to split the heat exchange in two sections. The solvent is sent to the top of a flash separator where it contacts with the hot stripped CO_2 in a packing section. The bypass solvent temperature is varied in this configuration to optimize the value of equivalent work. The configuration is shown in **Error! Reference source not found.**. The onfiguration was optimized using Aspen Plus® Optimization and results of optimized values of temperature and bypass flow are shown in Table 18. Table 19 compares the configurations of cold and hot rich bypass with warm rich bypass for same operating conditions. Values of bypass flows were optimized for each case.

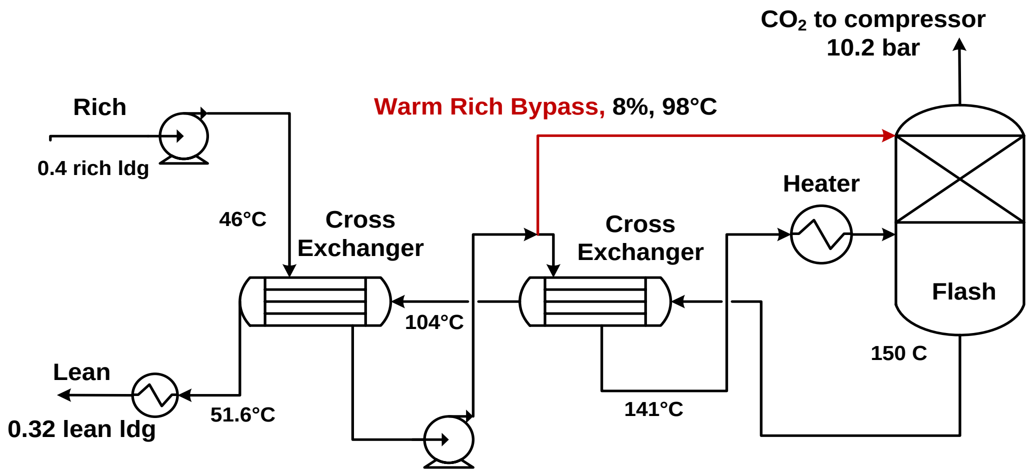

Figure 22: Advanced Flash Stripper – 1 with optimum values of operating conditions (8m PZ, 5°C LMTD, 150 bar compressor discharge pressure, Independence model)

Table 18: Equivalent work for advanced flash stripper – 1 (Independence model, variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C LMTD non-flashing cross exchanger, 2.5m Mellapak 250X packing)

Lean loading	**Optimum bypass flow**	**Optimum bypass Temperature**	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Total Equivalent Work**
mol/mol alk	%	°C	kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.26	27	120.9	104.7	21.76	10.43	32.88
0.29	14	105.6	100.0	20.54	9.64	31.26
0.32	**8**	**97.8**	**99.0**	**20.18**	**8.65**	**30.72**
0.34	5	111.1	106.2	21.56	7.87	32.50

Table 19: Equivalent work for advanced flash stripper – 1 (Independence model, variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C LMTD non-flashing cross exchanger, 2.5m Mellapak 250X packing)

Lean loading	**Cold Rich Bypass (Bypass from upstream of first CX, at 46°C)**		**Hot Rich Bypass (Bypass downstream of second CX, ~140°C)**		**Warm Rich Bypass (Bypass between two CX, ~120°C)**	
	Equivalent Work	Optimum % bypass	Equivalent Work	Optimum % bypass	Equivalent Work	Optimum % bypass
mol/mol alk	kJ/mol		kJ/mol		kJ/mol	
0.26	34.58	15	34.47	35	32.88	27
0.29	31.99	8	32.94	25	31.26	14
0.32	**31.27**	**4**	**32.54**	**18**	**30.72**	**8**
0.34	32.84	3	33.74	10	32.50	5

2. Advanced Flash Stripper 2 – This combination uses two bypass flows (hot/cold and hot/warm) and two packing sections to achieve more reversible heat recovery. Configurations are shown in Figure 23 and Figure 24. Configurations were optimized using Aspen Plus® Optimization and results of optimized values of temperature and bypass flow are shown in Table 20 for cold and warm and Table 21 for cold and hot.

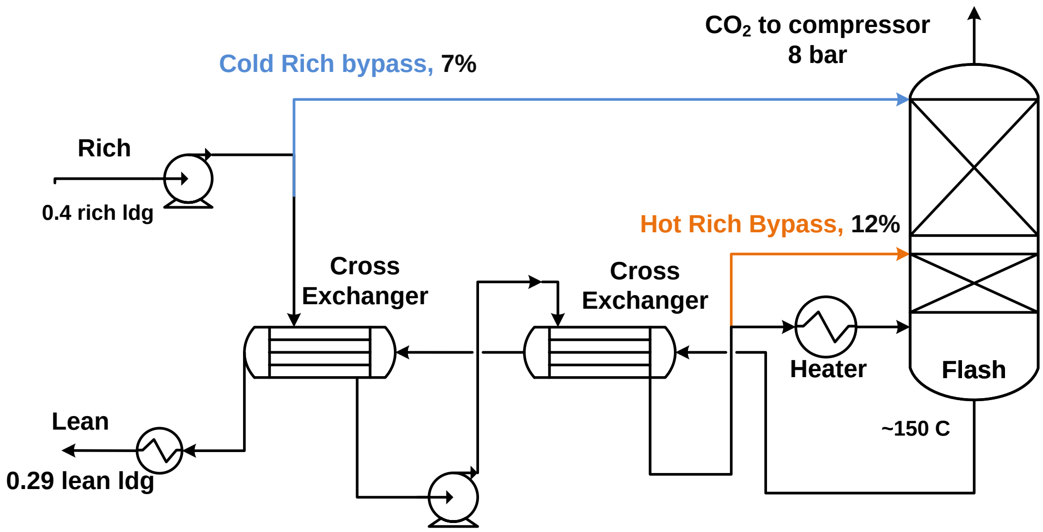

Figure 23: Advanced Flash Stripper – 2a with optimum values of operating conditions (Independence model, variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C LMTD non-flashing cross exchanger, 5m Mellapak 250X packing)

Table 20: Equivalent work for advanced flash stripper – 2a (Cold and Hot rich bypass, Independence model, variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C LMTD non-flashing cross exchanger)

Lean loading	**Optimum Cold Bypass**	**Optimum Hot Bypass**	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Total Equivalent Work**
mol/mol alk	%	%	kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.26	11	20	99.8	20.66	10.44	31.79
0.29	**7**	**12**	**96.5**	**19.78**	**9.65**	**30.50**
0.32	4	10	97.9	19.96	8.66	30.51
0.34	2	13	103.9	21.17	7.88	32.11

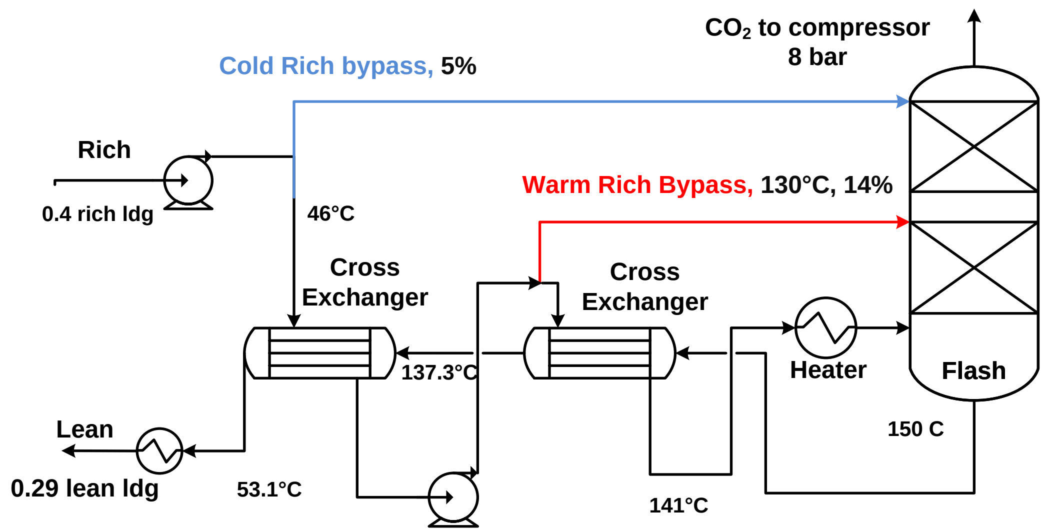

Figure 24: Advanced Flash Stripper – 2b with optimum values of operating conditions (Independence model, variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C LMTD non-flashing cross exchanger, 5m Mellapak 250X packing)

Table 21: Equivalent work for advanced flash stripper – 2b (Independence model, variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C LMTD non-flashing cross exchanger, 5m Mellapak 250X packing)

Lean loading	**Optimum Cold Bypass**	**Optimum Warm Bypass**	**Optimum Warm Bypass T**	**Heat Duty**	**Reboiler Equivalent Work**	**Compression Work**	**Total Equivalent Work**
mol/mol alk	%	%	°C	kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.26	8	18	126.5	100.2	20.73	10.43	31.85
0.29	**5**	**14**	**129.8**	**95.2**	**19.55**	**9.66**	**30.28**
0.32	3	15	135.9	97.5	20.00	8.66	30.54
0.34	2	15	137.6	103.9	21.28	7.87	32.22

3. Advanced Flash Stripper 3 – This combination uses all three possible temperature levels for heat recovery corresponding to cold, warm and hot rich bypass. Configuration is shown in Figure 25. Results of optimized cases are given in Table 22.

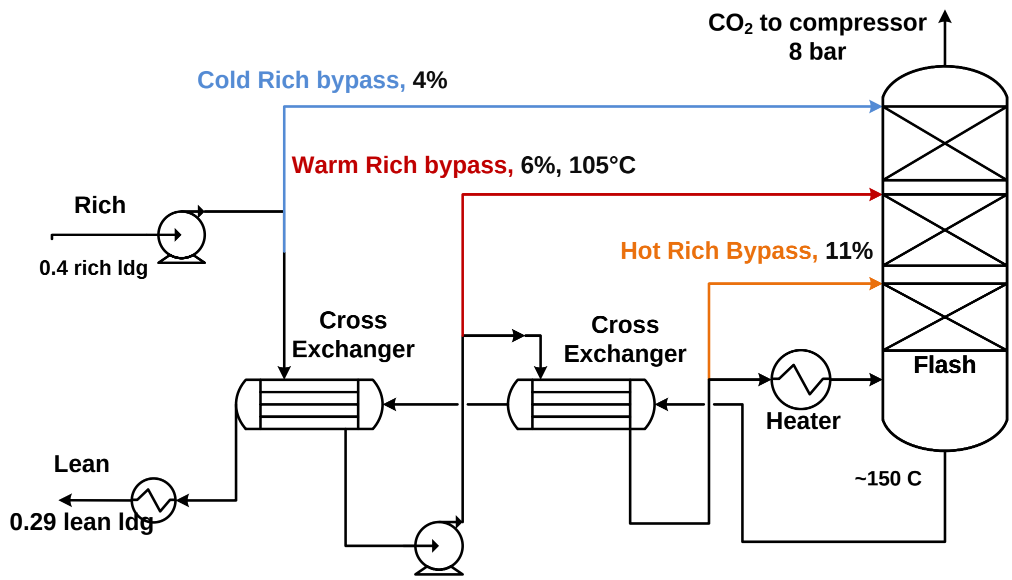

Figure 25: Advanced Flash Stripper – 3 with optimum values of operating conditions (Independence model, variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C LMTD non-flashing cross exchanger, 7.5m Mellapak 250X packing)

Table 22: Equivalent work for advanced flash stripper – 3 (cold, hot and warm rich bypass, Independence model, variable lean loading, 8m PZ, 0.4 rich loading, 150°C stripper T, 5°C LMTD non-flashing cross exchanger, 7.5m Mellapak 250X packing)

Lean loading	**Optimum Cold Bypass**	**Optimum Warm Bypass**	**Optimum Hot Bypass**	**Warm Bypass T**	**Heat Duty**	**Reboiler Eq. Work**	**Comp Work**	**Total Equivalent Work**
mol/mol alk	%	%	%	°C	kJ/mol	kJ/mol	kJ/mol	kJ/mol
0.26	7	8	14	89	97.9	20.24	10.43	31.36
0.29	**4**	**6**	**11**	**105**	**93.4**	**19.17**	**9.65**	**29.89**
0.32	2	3	10	94	95.9	19.57	8.65	30.12
0.34	2	3	9	115	102.3	20.84	7.87	31.78

3.2.3 Results

Figure 26 compares the equivalent work values for various complex configurations of Advanced Flash and Simple Stripper over a range of lean loadings.

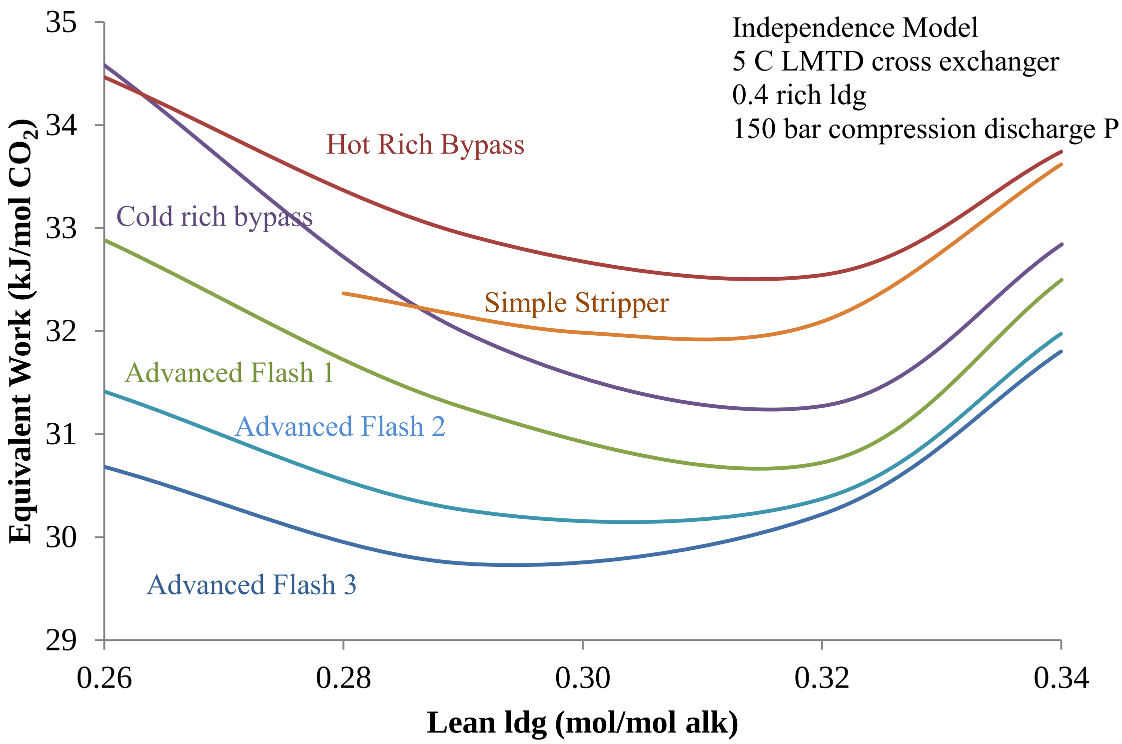

Figure 26: Equivalent work comparison of Advanced Flash Stripper configurations with Simple Stripper (8m PZ)

Table 23 shows the improvement of advanced flash as compared with the base case of simple stripper.

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Table 23: Equivalent work comparison of Advanced Flash Stripper configurations with Simple Stripper (8m PZ, 150 bar compressor discharge pressure, Independence model, 150°C stripping T, 5°C LMTD)

Configuration	**Equivalent Work ($kJ/mol\ CO_2$)**	**Improvement over base case**
Simple Stripper (Fawkes)	32.6	-
Interheated Stripper (Fawkes)	30.0	-
Simple Stripper (Independence, Base case)	32.1	-
Advanced Flash 1	30.8	4%
Advanced Flash 2	30.3	5.6%
Advanced Flash 3	29.8	7.1%

3.3 Pilot Plant configurations

The existing solvent regeneration configuration in the pilot plant facility comprising of two stage flash in University of Texas at Austin was evaluated for required modifications to adapt Advanced Flash Stripper. This design changed some aspects of previous modeling to take into consideration some practical design elements like fixed packing height and utilization of cross exchanger instead of cold rich bypass.

Following changes over the base design were made for modeling pilot plant configurations.

1. Flashing allowed in the cross exchanger (Process specification of 5°C LMTD in first cross exchanger and stream after first cross exchanger at bubble point)
2. Heat Recovery from hot CO_2 using a rich bypass exchange (heat exchanger instead of cold rich bypass) to minimize packing requirement
3. Fixed amount of packing (Multiple cases – 1m/2m/5m)
4. Multiple packing types (Structured/Random)

5. Other specifications: 8m PZ, 0.4 rich ldg, 0.29/0.27 lean ldg, 150 °C stripping Temperature

3.3.1 Cold Rich Bypass configuration

Figure 27 shows cold rich bypass evaluated for the pilot plant. The Heat Recovery Exchanger was designed for various values of LMTD. 5m of Mellapak 250X packing was used in the flash vessel for all the cases.

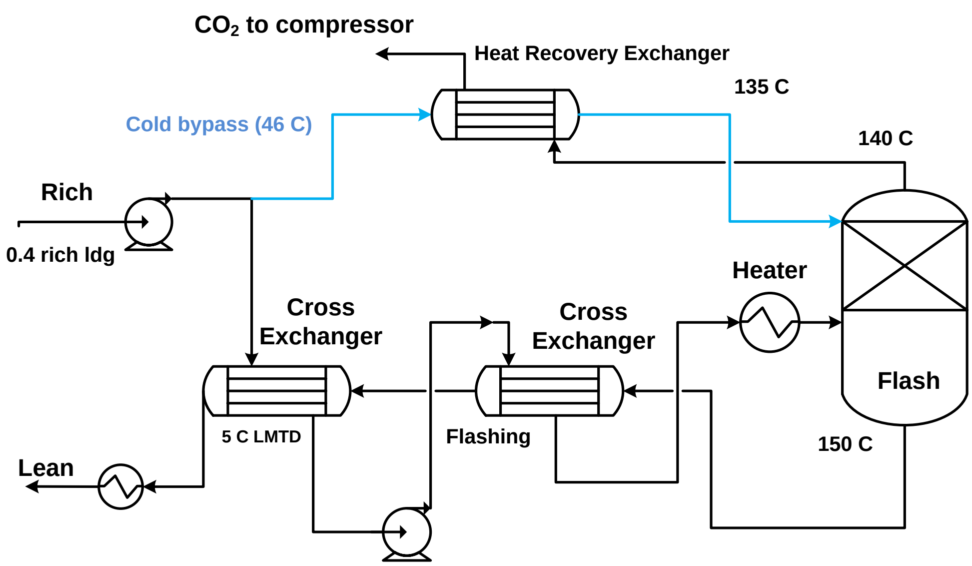

Figure 27: Cold rich bypass configuration for pilot plant (Independence model, 0.29 lean ldg, 8m PZ, 5m Mellapak 250X packing)

3.3.1.1 Sensitivity Analysis on cold rich bypass exchanger design

Cross exchanger used for heat recovery between cold rich solvent and hot CO_2 product was evaluated with the following specifications

1. 15°C LMTD

2. 20°C LMTD – This specification has an advantage of lower capital cost when compared with the above specification, with an associated penalty of higher energy requirement.

Selection of these numbers was based on effect of this design specification on total equivalent work as seen in Figure 28. There is a diminishing rate of return with a decrease in LMTD from 15 to 10 and even further from 10 to 5. To keep capital cost low, LMTD of 15 and 20°C were selected for further review.

Figure 28 and Table 24 shows the tradeoff between UA (estimation of capital cost was beyond the scope of this work) and equivalent work.

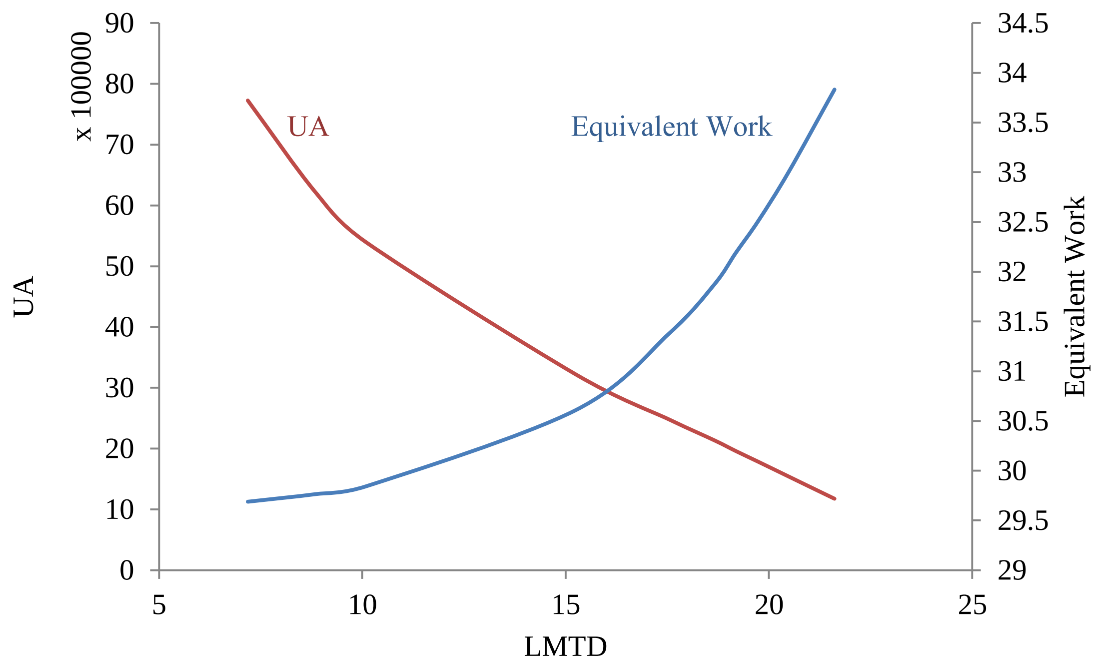

Figure 28: Sensitivity analysis of equivalent work with LMTD of cold rich bypass heat exchanger (configuration of cold rich bypass, Independence model, 0.4/0.29 rich/lean loading, 150°C stripper T, 5°C LMTD flashing cross exchanger, 5m Mellapak 250X packing)

Table 24: Equivalent work of cold rich bypass with different values of LMTD of cold rich bypass heat exchanger (Independence model, 0.4/0.29 rich/lean loading, 150°C stripper T, 5°C LMTD flashing cross exchanger, 5m Mellapak 250X packing)

LMTD °C	**Equivalent Work kJ/mol CO_2**
7.2	29.7
8.9	29.8
10.1	**29.8**
15.2	**30.6**
17.6	31.4
18.7	31.9
19.2	32.2
19.7	**32.5**
20.5	33.0
21.6	33.8

There was a marginal increase in equivalent work with an increase in LMTD from 10 to 15°C, while increase from 15 to 20°C caused even higher increase in equivalent work. For rest of the analysis, two cases of 15 and 20°C were selected as practical values for cross exchanger design LMTD.

3.3.2 Warm Rich Bypass configuration

Figure 29 shows the configuration of warm rich bypass evaluated for pilot plant. Structured packing (Mellapak 250X) was used for all cases with variable height of 2m and 5m.

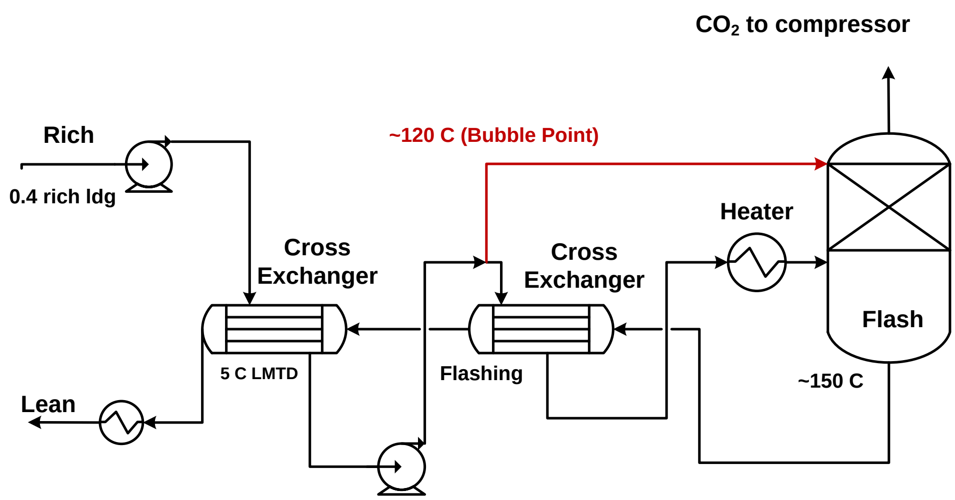

Figure 29: Warm rich bypass configuration for pilot plant (Independence model, 0.4/0.29 rich/lean loading, 150°C stripper T, 5°C LMTD flashing cross exchanger, 5m Mellapak 250X packing)

3.3.2.1 Sensitivity Analysis on packing height

A higher amount of packing provides more area for mass transfer in the stripper resulting in lower value of equivalent work. Following packing heights were evaluated.

1. Mellapak 250X – 5m and 2m

Figure 30 and Table 25 shows the comparison of equivalent work for 5m and 2m Mellapak 250X packing for this configuration.

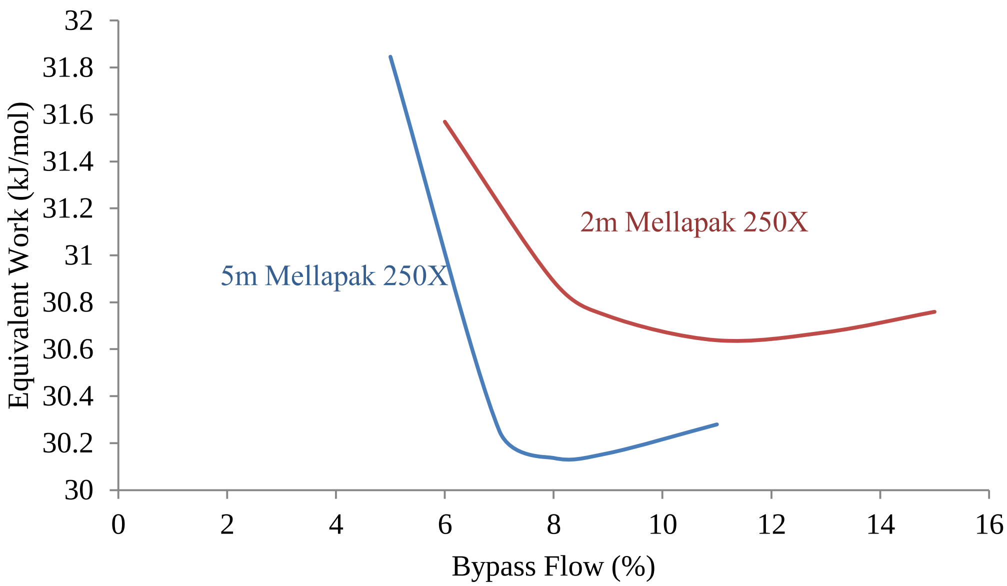

Figure 30: Equivalent work for 5m and 2m of packing for warm rich bypass configuration (Independence model, 0.29 lean ldg, 8m PZ, Mellapak 250X packing)

There is an energy penalty of only 0.5 kJ/mol with decrease in packing height from 5m to 2m. For the pilot scale operation, it is important for practical, structural and installation purpose to keep the packing requirement as minimum as possible, and hence 2m was selected for further analysis.

Table 25: Equivalent work for 5m and 2m Mellapak 250X packing for warm rich bypass configuration (8m PZ, 150 bar compressor discharge pressure, Independence model)

Bypass Flow (%)	**Equivalent Work (5m packing)**	**Bypass Flow (%)**	**Equivalent Work (2m packing)**
5	31.8	8	30.9
8	**30.1**	**11**	**30.6**
11	30.3	15	30.8

3.3.3 Cold and Warm Rich Bypass configuration

Figure 31 shows the configuration of cold and warm rich bypass. Cold rich bypass cross exchanger was designed for both 15°C and 20°C LMTD based on analysis of results for the previous configuration and 5m/2m packing height. Other than structured packing, random packing of CMR no.1 was also evaluated. A special case of 1m packing height was also evaluated. Configurations were optimized using Aspen Plus® Optimization. Results are shown in Table 26 and Table 27.

3.3.3.1 Packing Type sensitivity analysis

Following packing types were evaluated

1. Mellapak 250X (Structured packing) – Evaluated with 5m and 2m height
2. CMR No.1 (Random packing) – This packing is expected to have a lower capital and installation cost as compared to structured packing. It was evaluated with 2m and 1m.

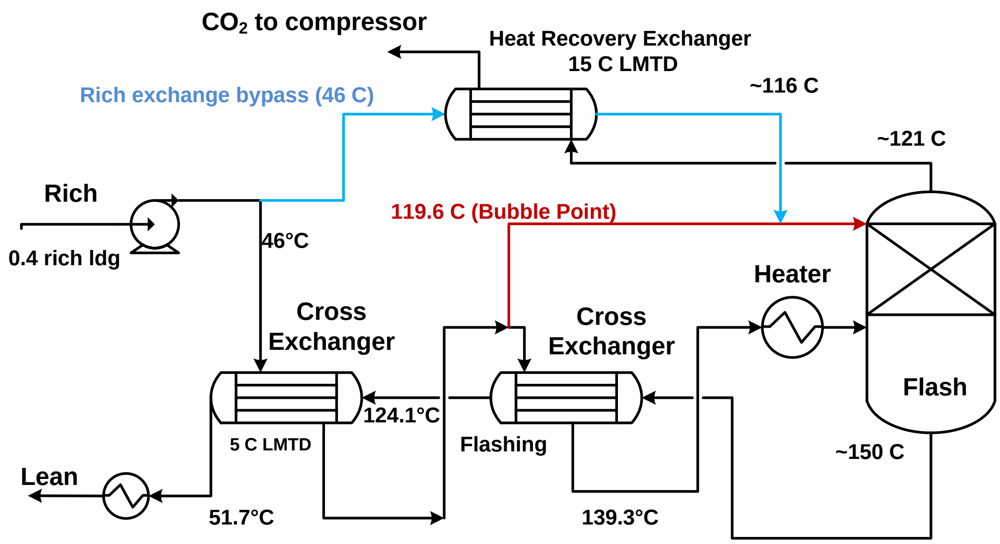

Figure 31: Cold and warm rich bypass configuration for pilot plant (Independence model, 0.29 lean ldg, 8m PZ, 5m Mellapak 250X packing)

Table 26: Equivalent work for Cold and Warm Rich bypass for Mellapak 250X packing (8m PZ, 0.4/0.29 rich/lean ldg, 5°C LMTD flashing cross exchanger, 150 bar compressor discharge pressure, Independence model)

Packing Height	**Cold Rich Cross Exchanger LMTD**	**Optimum Cold Bypass**	**Optimum Warm Bypass**	**Total Equivalent Work**
M	°C	%	%	kJ/mol
5	15	4	16.1	29.00
5	20	2.6	15.8	29.37
2	15	4	25.3	29.39
2	20	3	25	29.75

Table 27: Equivalent work for Cold and Warm Rich bypass for CMR No.1 packing (8m PZ, 0.4/0.29 rich/lean ldg, 5°C LMTD flashing cross exchanger, 150 bar compressor discharge pressure, Independence model)

Packing Height	**Cold Rich Cross Exchanger LMTD**	**Optimum Cold Bypass**	**Optimum Warm Bypass**	**Total Equivalent Work**
M	°C	%	%	kJ/mol
2	15	4	25	29.29
2	20	4	25	29.66
1	15	3.6	25	29.85
1	20	3.6	25	30.47

3.3.4 Other Configurations

Two other configurations of cold & hot bypass (Figure 33) and cold, hot and warm rich bypass (Figure 33) were also analyzed. The best case of 15°C LMTD heat recovery exchanger and 5m packing was evaluated for this configuration.

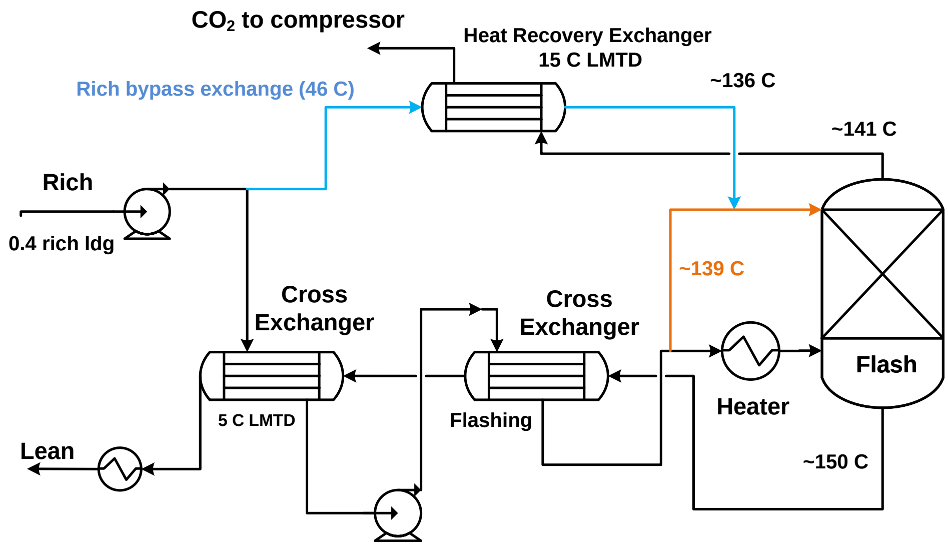

Figure 32: Cold and Hot rich bypass configuration for pilot plant (Independence model, 0.29/0.27 lean ldg, 8m PZ, 5m Mellapak 250X packing)

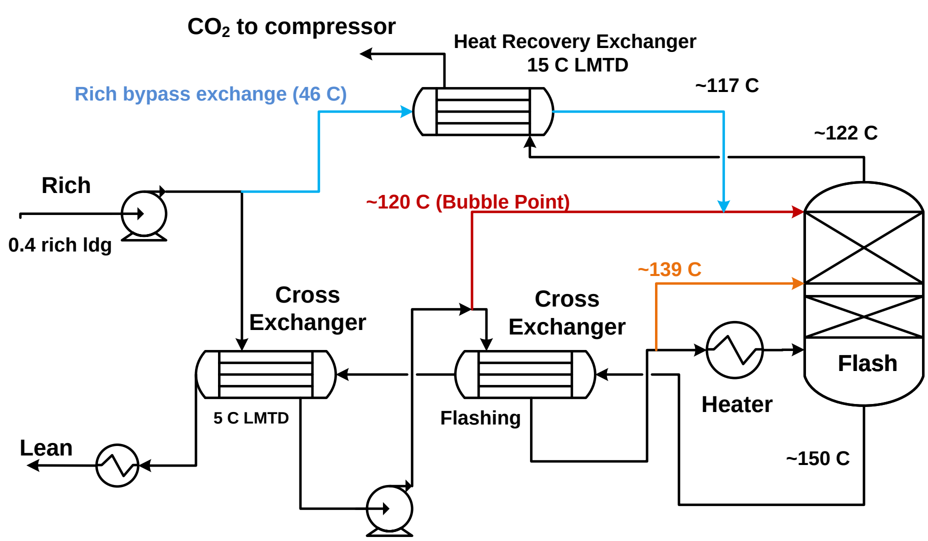

Figure 33: Cold, Warm and Hot rich bypass configuration for pilot plant (Independence model, 0.29/0.27 lean ldg, 8m PZ, 5m Mellapak 250X packing)

Table 28 gives the equivalent work values for the two cases with lean loading of 0.29 and 0.27. There was no major benefit of using additional bypass.

Table 28: Equivalent work comparison of other Advanced Flash Stripper configurations (8m PZ, 150 bar compressor discharge pressure, Independence model)

Configuration	**Equivalent Work @0.29 lean ldg ($kJ/mol\ CO_2$)**	**Equivalent Work @0.27 lean ldg ($kJ/mol\ CO_2$)**
Cold and Hot bypass	30.0	30.3
Cold, warm and hot bypass	29.0	29.1

3.3.5 Results

Table 29 summarizes the optimum value of equivalent work for all the pilot plant configurations evaluated in this work for 15°C LMTD heat recovery cross exchanger, rich/lean loading of 0.4/0.29 and 5m Mellapak 250X packing as best case from energy requirement point of view.

Table 29: Optimum value of equivalent work for all advanced flash stripper cases using cold rich heat recovery exchanger for pilot plant (Independence Model, 8m PZ, 0.4 rich ldg, 5m Mellapak 250X packing)

Configuration	**Equivalent Work @0.29 lean ldg ($kJ/mol\ CO_2$)**
Warm bypass	30.1
Cold and Hot bypass	30.0
Cold and Warm bypass	**29.0**
Cold, warm and hot bypass	29.0

The configuration of cold and warm rich bypass had the best performance and a summary of all the cases evaluated for that configuration is given in Figure 34 for Mellapak 250X and Figure 35 for CMR No.1.

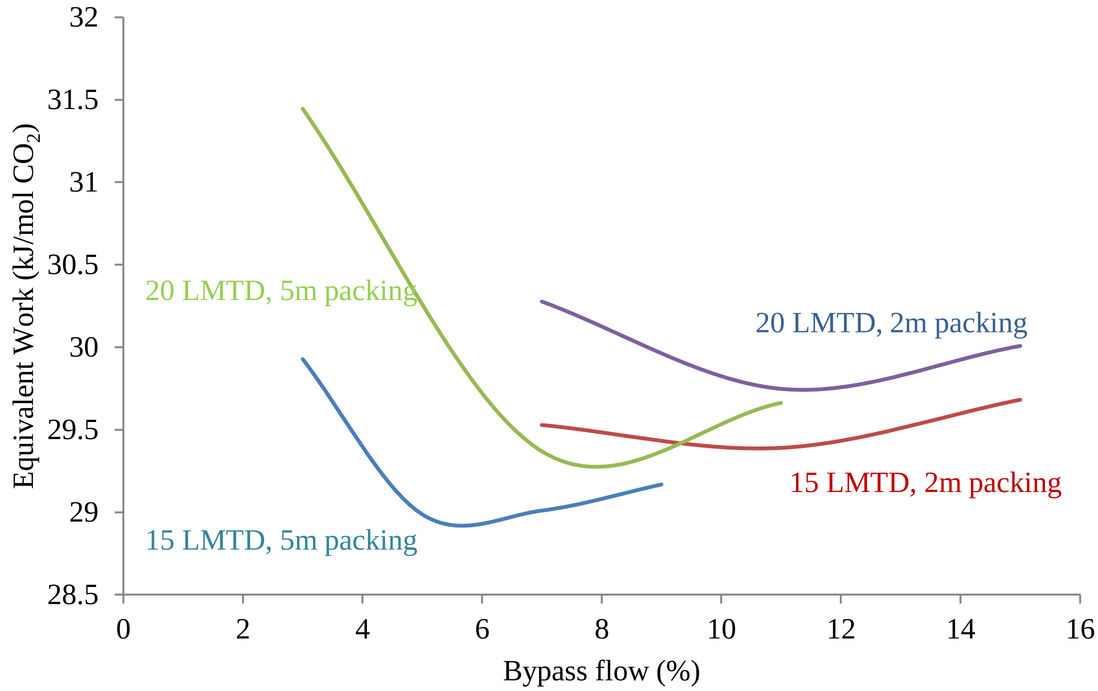

Figure 34: Equivalent Work for Cold (using heat exchange) and Warm rich bypass configuration for multiple values of heat exchange LMTD and packing height, Mellapak 250X packing (Independence model, 0.29 lean ldg, 8m PZ)

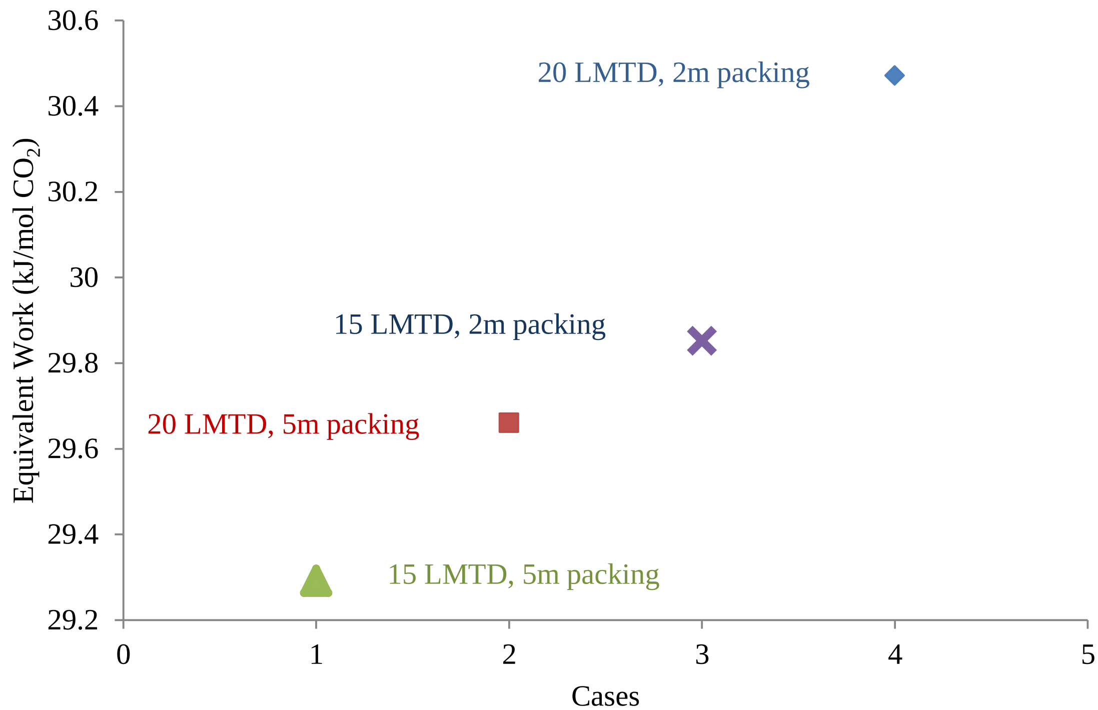

Figure 35: Equivalent Work for Cold (using heat exchange) and Warm rich bypass configuration for multiple values of heat exchange LMTD and packing height, CMR No.1 packing (Independence model, 0.29 lean ldg, 8m PZ)

3.4 CONCLUSIONS

1. The advanced flash stripper had the best performance of 29.8 kJ/mol (with packing) and 29.0 kJ/mol with cold rich heat recovery exchanger. This makes it the best stripper configuration evaluated so far.
2. The best configuration alternative is cold and warm rich bypass with marginal benefit of additional temperature level bypass beyond that.
3. Random packing provides comparable performance to structured packing with 29.3 kJ/mol equivalent work.

Chapter 4: Modeling of Pilot Plant Data

This chapter summarizes the modeling and simulation work for the Fall 2011 pilot plant campaign of the Carbon Capture Pilot Plant Project at the University of Texas at Austin. Pilot plant experiments were conducted on a 0.1 MW scale to demonstrate the performance of concentrated (8m) piperazine. Previous campaigns have demonstrated the superiority of piperazine as a solvent for amine scrubbing. The Winter 2011 campaign data was also used to validate the 5deMayo solvent model (Hilliard, 2008).

The Fawkes model was available and used for simulation of Fall 2011 campaign operating cases (Frailie et al., 2011). Vapor liquid equilibrium analysis of Winter and Fall 2011 campaigns was done and rigorous reconciliation of Fall 2011 data was done using Aspen Plus® Data Fit. Optimization of the pilot plant configuration was done using the validated model to quantify the minimum value of equivalent work possible in the pilot plant configuration.

4.1 INTRODUCTION

Four pilot plant campaigns have been carried out at the Separations Research Program (SRP) at UT Austin using concentrated (8 m) PZ to absorb 90% CO_2 from air (with 12% CO_2). The SRP pilot plant uses an absorber-stripper configuration corresponding to a 0.1 MW coal-fired power plant (Seibert et al., 2011).

4.1.1 Winter 2011 Campaign

The winter 2011 campaign was performed with regeneration by the two stage flash. The 5deMayo model was validated using the operating conditions of this campaign and the validated model was used for further analysis. This work uses the data of the campaign for vapor liquid equilibrium analysis to analyze the solvent performance over the two campaigns.

4.1.2 Fall 2011 Campaign

The Fall 2011 pilot plant campaign used solvent regeneration by a heated two-stage flash with cold rich bypass as shown in Figure 36. The LP cross exchanger was used only in a few steady state runs. This work uses the measured operating conditions of the stripping section and laboratory measurements of solvent composition to validate the solvent model, demonstrate the expected energy performance at pilot scale, and quantify expected improvement at optimum operating conditions.

For this campaign, the 2-stage flash was modified to allow some solvent to bypass the cross exchanger and high pressure flash vessel and to contact directly with vapor coming out from the low pressure vessel. This modification, cold rich bypass, helps in heat recovery as some of the water vapor evaporating with CO_2 condenses as it contacts this cold solvent (Van Wagener, 2011).

10 steady state runs were carried out during the Fall campaign. Each steady state run roughly corresponded to a period of 2 hours during which major operating conditions remained approximately constant. Mean and Standard Deviation for each operating parameter was recorded for each steady state.

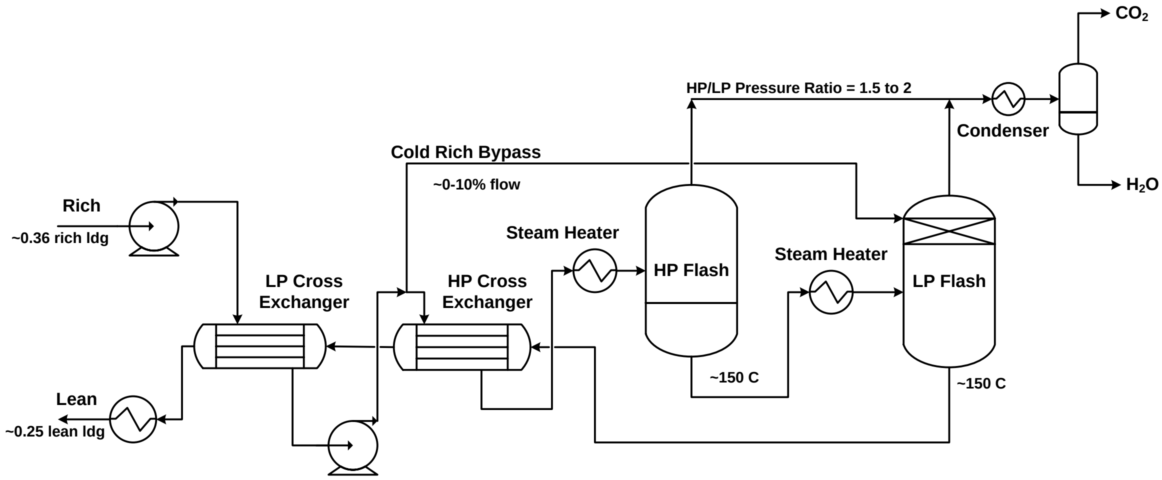

Figure 36: Two-stage flash configuration used in Winter and Fall 2011. Cold rich bypass used only in Fall 2011.

Figure 37 shows the various measurements taken in the stripper section of the pilot plant configuration and Table 30 shows the values of the measurements for the Fall campaign.

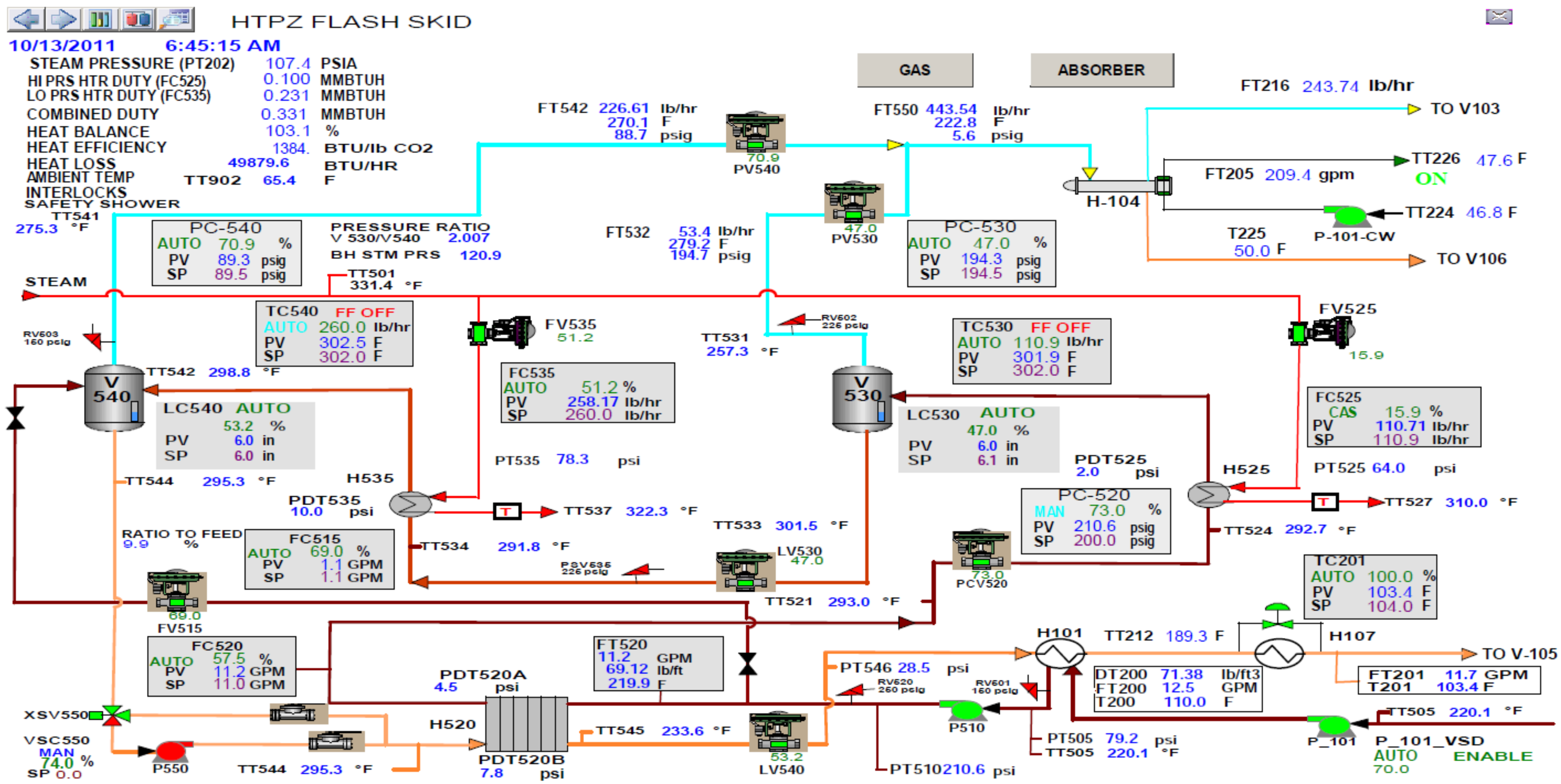

Figure 37: Measurements taken in regeneration section of pilot plant configuration

Table 30: Measurements of various operating variables in solvent regeneration during Fall 2011 campaign

Variable	Tag	Units	1	2	3	4	5	6	7	8	9	10	11
Rich Flow	FT520	lb/h	6713	6693	6086	6033	6697	6126	8268	8300	9237	9264	11960
Cold Rich Bypass	FT515	lb/h	0.0	0.0	600.5	665.3	31.6	609.2	827.6	600.3	640.5	642.7	831.3
Lean Flow	FT201	lb/h	6359	6359	6432	6437	6408	6476	8694	8579	9470	9503	12316
Rich loading	Lab		0.344	0.333	0.345	0.350	0.339	0.351	0.338	0.340	0.344	-	0.351
Semi-rich loading	Lab		0.294	0.297	0.312	0.298	0.291	0.296	0.287	0.292	0.304	-	0.292
Lean loading	Lab		0.253	0.250	0.256	0.259	0.248	0.258	0.245	0.249	0.255	0.256	0.259
Rich T	TT200	F	-	100.2	-	107.1	109.3	110.0	111.6	100.2	99.34	99.65	104.78
Rich Heater T	TT505	F	103.59	109.57	105.86	218.84	197.21	219.54	245.69	99.14	98.37	98.69	103.63
Pump suction P	PT505	psig	9.3	8.9	9.2	80.3	78.8	79.2	68.6	5.60	4.42	4.47	7.25
Pump discharge P	PT510	psig	150.21	153.32	172.37	181.05	185.91	209.55	201.38	178.36	180.52	180.80	193.73
CX Rich Inlet T	TT520	F	104.76	110.66	107.07	224.44	202.15	224.44	248.67	100.28	99.24	99.52	104.82
CX Rich Outlet T	TT521	F	277.99	279.56	286.57	290.50	288.26	293.00	290.92	286.25	282.77	282.03	280.33
CX Lean Inlet T	TT544	F	295.30	295.49	294.92	293.08	294.48	295.23	292.07	298.30	295.74	295.06	294.25

Variable	**Tag**	**Units**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
CX Lean Outlet T	TT545	F	124.02	129.00	135.24	233.50	209.92	233.22	259.57	128.17	127.34	127.75	133.17
HP Heater T	TC530	F	301.68	301.77	301.79	301.80	301.61	301.86	303.82	301.80	301.82	301.64	301.74
HP Flash P	PC530	psig	134.91	139.20	145.99	140.02	138.47	194.49	185.07	164.06	164.06	164.02	164.11
HP Flash liq. T	TT533	F	301.38	301.37	301.34	301.49	301.38	301.56	303.48	301.50	301.05	301.05	301.62
HP Vapor T	TT532	F	286.85	285.52	285.88	286.92	287.41	279.14	280.98	283.23	281.47	281.53	287.01
HP Vapor Flow	FT532	lb/h	183.30	153.05	155.76	167.78	183.95	53.45	53.86	90.48	115.92	116.81	179.61
LP Heater T	TC540	F	302.33	303.10	306.28	301.90	301.69	302.63	303.17	303.74	300.80	300.15	298.83
LP Flash P	PC540	psig	85.01	88.47	92.00	87.99	87.45	89.51	85.98	86.50	79.97	79.98	79.90
LP Flash drum T	TT542	F	-	-	-	297.15	298.78	298.76	300.9	301.7	298.31	298.14	296.41
LP Flash liq. T	TT544	F	295.30	295.49	294.92	293.08	294.48	295.23	292.07	298.30	295.74	295.06	294.25
LP Vapor T	TT541	F	299.45	299.85	222.83	254.27	295.53	275.37	287.44	255.25	262.04	257.83	245.35
LP Vapor Flow	FT542	lb/h	220.88	212.15	118.63	125.00	191.62	225.44	365.48	233.89	314.57	294.40	317.42
Combined Vapor	FT550	lb/h	542.76	512.13	405.03	420.16	422.88	443.43	588.32	496.54	575.11	568.85	626.68
Stripped CO_2	FT216	lb/h	254.18	238.13	246.00	241.61	244.69	246.73	314.17	309.36	368.36	367.45	446.71

4.2 VAPOR LIQUID EQUILIBRIUM ANALYSIS

CO_2 solubility in PZ at high pressure and temperature was studied by Xu, who developed a vapor liquid equilibrium model for PZ-CO_2-H_2O using total pressure measurement (Xu et al., 2011). Equation 3 gives the empirical model for CO_2 partial pressure in this system, dependent on temperature and loading.

$$\ln P_{CO_2}\,(Pa) = 35.3 - 11054\,\frac{1}{T} - 18.9\alpha^2 + 4958\frac{\alpha}{T} + 10163\frac{\alpha^2}{T}$$

Equation 3: Partial Pressure of CO_2 in loaded PZ solution

Vapor liquid equilibrium approach in both flash vessels was studied. Partial pressure of CO_2 was calculated using Equation 3. Equation 4 was used to calculate H_2O partial pressure (Moore et al., 1969). Total equilibrium pressure was calculated by adding these two. PZ was assumed to be negligible in the vapor phase.

$$\ln P_{H_2O} = A + \frac{B}{T} + C\ln T + DT^E$$

$$A = 7.3469E + 01$$

$$B = -7.2582E + 03$$

$$C = 7.3037\,E + 00$$

$$D = 4.1653E - 06$$

$$E = 2$$

Equation 4: Partial Pressure of water

There are 3 different values of measured temperature which could be used in above equations, temperature of inlet solvent, temperature of liquid inside the vessel (only available in low pressure vessel), and temperature of liquid outlet. Temperature measurement of liquid inside the flash was assumed to be the most accurate representation and was used for equilibrium calculations in the low pressure flash. For the high pressure vessel, temperature of the liquid outlet was assumed to be a closer representation of actual temperature inside the vessel and was used for this analysis. Also, the temperature difference between inlet and outlet liquid was found to be negligible (less than 0.5 ºF).

Loading measurements were carried out for each steady state run using manual and auto titration for measuring CO_2 and PZ concentration in the solvent at various points in the process. Both these values were used to calculate the CO_2 partial pressure. The auto-titration values were more erratic and had less systematic variation than manual titration values. Hence, manual titration values were used for this analysis.

The ratio of estimated equilibrium to measured pressure was calculated for each run as given in Figure 38 and Figure 39. The equilibrium pressure measurements are prone to error, mainly due to lab measurement errors. While the standard deviations found in the lab measurements were smaller (<0.5% for most cases), the error propagates to higher values in the total pressure equation due to the exponential form of Equation 3. Any measurement errors in temperature were ignored to keep the analysis simpler, and by assuming that major error in the calculation was due to loading measurement. Total pressure measurements were in good agreement with the pressures predicted by VLE equations. The high error values are denoted by the calculated error bars on each value in the figures.

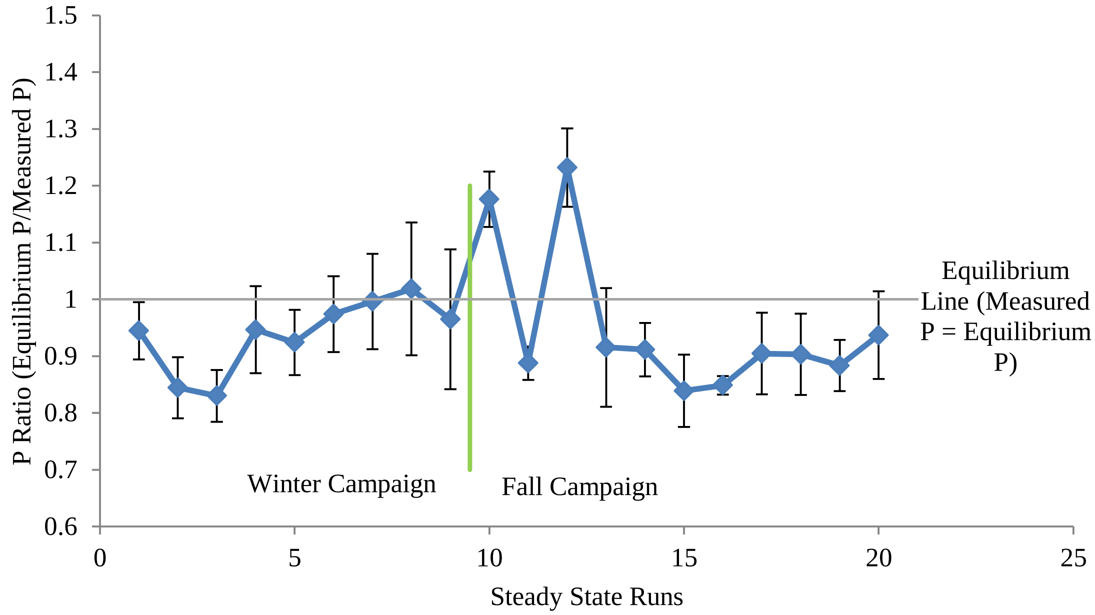

Figure 38: Deviation of measured pressure in HP flash vessel from equilibrium pressure for each steady state run in Winter and Fall campaigns

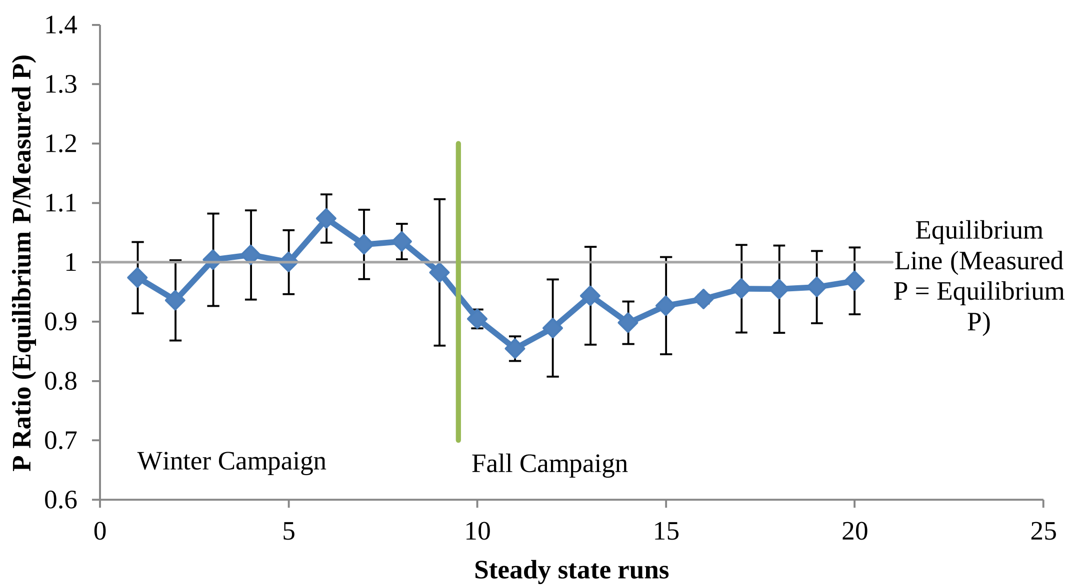

Figure 39: Deviation of measured pressure in LP flash vessel from equilibrium pressure for each steady state run in Winter and Fall campaigns

Disagreement of measured pressure with the model can be attributed to one of these factors:

- Inaccuracies in loading, T, or P measurements;
- Inaccuracies in the solvent model.

These were further studied with rigorous reconciliation in Aspen Plus®.

4.3 RIGOROUS DATA RECONCILIATION

4.3.1 Methodology

Previous work has used the concept of mean absolute percentage error to quantify the deviation of model from the observed data (Van Wagener, 2011). It is defined as

$$MAPE = \frac{1}{n}\sum_{i=1}^{N}\left|\frac{S_i - M_i}{M_i}\right|.100\%$$

Equation 5: Mean Average Percentage Error between measured and simulated values

Data reconciliation for the Fall campaign was done using the Data Fit function of Aspen Plus® to minimize the objective function for each steady state run. The objective function is the sum of square of difference of measured and modeled values divided by standard deviation. Measured value and standard deviation were calculated by taking mean and standard deviation of values recorded at 2-minute intervals during each run. The following variables were selected to formulate the objective function.

- HP and LP Flash vapor flow
- CO_2 stripped from the system
- HP and LP heater duties
- Cross exchanger rich stream outlet T
- CO_2 in semi rich stream

- CO_2 and PZ in lean stream

The following variables were manipulated to minimize the objective function.

- Stream T from steam heater outlet
- Cross exchanger lean stream outlet T
- CO_2, PZ, and H_2O in inlet rich stream
- HP and LP flash vessel pressure

Following variables were adjusted from their original measured values

- HP and LP vapor flow – Measurements made by the instrument assumes a constant molecular weight of the gas. Observed vapor flow was adjusted to molecular weight calculated by Aspen Plus® for each steady state run.
- HP and LP Heat Duty – Calculated heat loss was subtracted from reported heat duty for each run. Heat loss for each run was estimated using **Error! eference source not found.** and was assumed to be equal for both heaters.

$$Q_{loss} = C(T_{heater} - T_{ambient})$$

Equation 6: Heat loss estimate for HP and LP heaters

C is a regressed parameter with value 350 BTU/h °C for this configuration (Van Wagener, 2011).

4.3.2 Previous Results

Previous reconciliation attempts using the 5deMayo model for the Winter 2011 campaign have shown high deviation for some of the operating parameters like HP and LP overhead flow. Table 31 shows the deviation in the values of these operating conditions which ranged from low values under 5% for many variables but up to 30% for some other variables.

Table 31: Mean Absolute Percentage Error for important variables for Winter 2011 campaign

Parameter	Average MAPE for campaign
Semirich ldg	2.1%
Lean ldg	3.3%
LP Flash T	0.9%
HP Flash T	1.2%
Stripped CO_2	4.7%
MAPE	2.9%
HP Overhead flow	30.6%
LP Overhead flow	17.2%

4.3.3 Fall 2011 Results

Table 32 shows the result of deviation between measured and observed values of parameters used in reconciliation. Absolute percentage error between the reconciled and observed value was calculated for each run along with an average value of absolute error as given in Table 33.

Table 32: Difference between measured and estimated values and deviation for each operating variable used in reconciliation of Fall 2011 campaign data

Variable/Run		**1**		**2**		**3**	
		Meas	Est	Meas	Est	Meas	Est
FT216	Value	254.18	251.51	238.13	229.58	246.00	239.63
	Deviation	1.41	1.04	1.95	1.39	1.31	0.83
FT532	Value	183.43	173.11	153.05	131.96	155.76	158.52
	Deviation	2.32	1.46	3.79	1.94	1.23	1.01
FT542	Value	220.88	224.59	212.15	235.22	118.63	127.33
	Deviation	1.58	1.04	2.67	1.76	1.03	0.70
PT530	Value	149.60	149.61	153.90	153.90	160.69	160.69
	Deviation	0.33	0.00	1.34	0.00	0.28	0.00
PT540	Value	99.71	99.74	103.17	104.27	106.70	106.86
	Deviation	0.12	0.12	0.90	0.61	0.12	0.12
HPDUTY	Value	237500	243318	213000	213548	169000	184840
	Deviation	3687	1665	3673	1932	3337	1363
LPDUTY	Value	171500	155859	172000	171966	196000	177285
	Deviation	1618	1066	51	51	1400	851
CX2T	Value	277.99	278.81	279.56	280.60	286.57	286.31
	Deviation	0.38	0.24	0.50	0.26	0.17	0.11
TT524	Value	279.16	278.81	281.17	280.61	284.39	284.65
	Deviation	0.32	0.23	0.34	0.26	0.12	0.10
TT534	Value	296.46	295.82	296.47	296.43	296.64	296.65
	Deviation	0.12	0.09	0.10	0.08	0.04	0.01
CO2SRMWT	Value	0.12	0.12	0.11	0.11	0.12	0.11
	Deviation	0.00	0.00	0.04	0.00	0.73	0.00
CO2MSWT	Value	599.65	640.69	581.21	617.57	585.95	616.59
	Deviation	5.04	1.08	2.44	1.14	5.92	1.58
HPHEATER	Value	301.68	300.97	301.77	301.72	301.79	302.97
	Deviation	0.24	0.10	0.18	0.08	0.15	0.11
LPHEATER	Value	302.33	304.56	303.10	306.11	306.28	307.68
	Deviation	0.15	0.09	0.19	0.07	0.12	0.08
CX1RT	Value	124.02	119.41	129.13	125.96	135.24	131.93
	Deviation	2.00	0.28	2.00	0.39	2.00	0.28
CO2CALC	Value	836.44	892.00	805.17	846.96	800.37	856.02
	Deviation	4.01	1.42	3.22	1.64	8.64	1.71
PZCALC	Value	2383.12	2377.10	2360.62	2340.85	2269.40	2261.87
	Deviation	2.86	1.96	3.30	2.19	5.22	3.53
H2OCALC	Value	3493.45	3534.32	3527.21	3690.71	3616.73	3629.57
	Deviation	17.47	14.48	17.64	16.51	8.32	8.20
PUPMPRES	Value	164.91	164.92	168.02	168.16	187.07	187.70
	Deviation	0.66	0.66	2.16	2.16	1.09	0.98

Variable/Run		4		5		6	
		Meas	Est	Meas	Est	Meas	Est
FT216	Value	241.61	240.36	244.69	236.91	246.73	231.00
	Deviation	1.77	0.76	23.07	5.32	1.21	0.58
FT532	Value	167.89	166.13	183.95	156.40	53.42	55.20
	Deviation	1.00	0.91	8.15	7.05	0.65	0.58
FT542	Value	124.98	145.52	191.61	212.04	225.45	245.79
	Deviation	1.28	0.55	14.71	3.67	1.42	0.68
PT530	Value	154.72	154.72	153.17	153.17	209.19	209.19
	Deviation	0.16	0.00	1.00	0.00	0.37	0.00
PT540	Value	102.69	103.36	102.15	99.80	104.21	104.72
	Deviation	0.15	0.14	0.57	0.49	0.18	0.16
HPDUTY	Value	150131	145130	186500	187184	75000	77874
	Deviation	2740	858	7580	7574	689	564
LPDUTY	Value	139395	134674	144500	140659	209000	204033
	Deviation	450	421	7580	3663	689	586
CX2T	Value	290.50	290.36	288.26	287.41	293.00	293.58
	Deviation	0.10	0.08	0.78	0.71	0.29	0.12
TT524	Value	286.96	286.92	285.26	284.80	292.76	292.89
	Deviation	0.07	0.06	0.63	0.63	0.12	0.07
TT534	Value	296.41	295.71	296.48	296.94	291.81	291.47
	Deviation	0.08	0.06	0.29	0.19	0.06	0.05
CO2SRMWT	Value	0.11	0.11	0.11	0.11	0.12	0.12
	Deviation	0.00	0.00	0.00	0.00	0.00	0.00
CO2MSWT	Value	610.23	631.92	585.69	626.42	607.45	638.97
	Deviation	3.42	1.96	2.58	1.47	3.89	1.20
HPHEATER	Value	301.80	301.04	301.61	302.10	301.86	301.47
	Deviation	0.14	0.06	0.32	0.20	0.12	0.05
LPHEATER	Value	301.90	304.57	301.69	304.77	302.63	304.96
	Deviation	0.11	0.05	0.27	0.17	0.14	0.05
CX1RT	Value	233.50	229.48	209.92	209.61	233.22	231.89
	Deviation	0.72	0.51	6.83	4.96	0.32	0.24
CO2CALC	Value	827.24	872.07	810.12	863.12	833.82	869.78
	Deviation	7.69	2.12	11.42	5.26	5.17	1.31
PZCALC	Value	2316.94	2275.33	2337.52	2336.43	2324.99	2311.01
	Deviation	9.96	5.39	0.94	0.66	4.88	3.07
H2OCALC	Value	3554.12	3553.92	3580.96	3587.14	3576.39	3599.69
	Deviation	15.28	15.28	3.58	3.56	7.51	7.19
PUPMPRES	Value	119.84	113.84	119.69	115.63	120.95	117.56
	Deviation	2.00	0.20	2.00	0.88	2.00	0.15

Variable/Run		7		8		9	
		Meas	Est	Meas	Est	Meas	Est
FT216	Value	314.17	281.42	309.36	295.92	368.36	350.19
	Deviation	2.72	1.29	1.59	0.89	5.94	2.30
FT532	Value	53.83	39.59	90.50	86.93	115.97	109.25
	Deviation	1.97	1.27	1.30	0.98	2.55	2.08
FT542	Value	365.55	375.98	233.91	274.32	314.62	337.76
	Deviation	5.08	2.27	4.05	1.09	8.34	3.38
PT530	Value	199.77	199.77	178.76	178.76	178.76	178.76
	Deviation	0.39	0.00	0.34	0.00	0.37	0.00
PT540	Value	100.68	100.18	101.20	102.32	94.67	95.29
	Deviation	0.21	0.19	0.21	0.19	0.28	0.25
HPDUTY	Value	120500	127869	158500	160319	214000	222300
	Deviation	3352	1570	471	453	2258	1631
LPDUTY	Value	292500	273327	294500	295553	335000	324432
	Deviation	3352	2172	984	893	4570	3169
CX2T	Value	292.07	292.15	286.25	287.03	282.77	282.99
	Deviation	0.18	0.12	0.32	0.12	0.29	0.17
TT524	Value	292.10	292.15	286.66	287.04	283.31	282.99
	Deviation	0.17	0.12	0.29	0.12	0.27	0.17
TT534	Value	293.49	295.33	294.40	293.94	292.41	292.34
	Deviation	0.28	0.10	0.11	0.08	0.15	0.09
CO2SRMWT	Value	0.12	0.12	0.11	0.12	0.12	0.12
	Deviation	0.00	0.00	0.00	0.00	0.00	0.00
CO2MSWT	Value	811.15	849.45	784.98	818.17	887.34	919.46
	Deviation	4.14	1.14	3.61	1.54	9.05	2.75
HPHEATER	Value	303.82	306.27	301.80	301.29	301.82	301.74
	Deviation	0.23	0.12	0.18	0.09	0.14	0.10
LPHEATER	Value	303.17	306.31	303.74	307.37	300.80	303.66
	Deviation	0.18	0.09	0.23	0.07	0.32	0.12
CX1RT	Value	259.57	259.61	128.17	122.43	127.34	122.05
	Deviation	1.38	0.98	0.36	0.14	0.61	0.22
CO2CALC	Value	1116.94	1130.62	1071.60	1113.82	1228.76	1269.34
	Deviation	1.34	1.07	7.93	1.75	12.41	3.00
PZCALC	Value	3232.58	3213.34	3088.40	3066.51	3496.64	3468.04
	Deviation	2.59	1.73	5.87	3.77	9.79	6.32
H2OCALC	Value	4746.08	4775.42	4740.30	4742.06	5152.10	5200.42
	Deviation	3.80	3.65	9.01	8.77	14.43	13.08
PUPMPRES	Value	121.41	119.74	193.06	193.16	195.22	195.29
	Deviation	2.00	0.20	0.45	0.45	0.67	0.67

Variable/Run		11	
		Meas	Est
FT216	Value	446.71	427.86
	Deviation	3.47	2.35
FT532	Value	179.74	173.60
	Deviation	3.96	2.77
FT542	Value	317.47	343.75
	Deviation	7.50	2.96
PT530	Value	178.81	178.81
	Deviation	0.48	0.00
PT540	Value	94.60	98.37
	Deviation	0.45	0.34
HPDUTY	Value	322500	354565
	Deviation	4893	2485
LPDUTY	Value	322500	332785
	Deviation	3267	2597
CX2T	Value	280.33	278.54
	Deviation	0.31	0.16
TT524	Value	280.34	278.54
	Deviation	0.29	0.16
TT534	Value	294.52	294.60
	Deviation	0.15	0.11
CO2SRMWT	Value	0.12	0.12
	Deviation	0.00	0.00
CO2MSWT	Value	1170.02	1210.82
	Deviation	6.20	2.99
HPHEATER	Value	301.74	301.86
	Deviation	0.21	0.12
LPHEATER	Value	298.83	302.73
	Deviation	0.34	0.10
CX1RT	Value	133.17	131.30
	Deviation	0.19	0.16
CO2CALC	Value	1593.68	1638.32
	Deviation	8.92	3.46
PZCALC	Value	4450.85	4410.50
	Deviation	11.57	7.14
H2OCALC	Value	6746.78	6746.78
	Deviation	17.54	16.96
PUPMPRES	Value	208.43	208.28
	Deviation	0.80	0.80

Table 33: Deviation between measured and reconciled values for all variables used in data reconciliation of Fall 2011 campaign

FT 216	FT 532	FT 542	PT 530	PT 540	HP Duty	LP Duty	CX Temp	TT 524	TT 534	CO_2 Semi	CO_2 Lean	PZ Lean	HP Htr T	LP Htr T	CX T	CO_2 Rich	PZ Rich	H_2O Rich	Pump P
1.0%	5.6%	1.7%	0.0%	0.0%	2.4%	9.1%	0.3%	0.1%	0.2%	4.0%	6.8%	0.3%	0.2%	0.7%	3.7%	6.6%	0.3%	1.2%	0.0%
3.6%	13.8%	10.9%	0.0%	1.1%	0.3%	0.0%	0.4%	0.2%	0.0%	0.7%	6.3%	0.8%	0.0%	1.0%	2.5%	5.2%	0.8%	4.6%	0.1%
2.6%	1.8%	7.3%	0.0%	0.1%	9.4%	9.5%	0.1%	0.1%	0.0%	6.7%	5.2%	0.3%	0.4%	0.5%	2.4%	7.0%	0.3%	0.4%	0.3%
0.5%	1.0%	16.4%	0.0%	0.6%	3.3%	3.4%	0.0%	0.0%	0.2%	2.5%	3.6%	1.8%	0.3%	0.9%	1.7%	5.4%	1.8%	0.0%	5.0%
3.2%	15.0%	10.7%	0.0%	2.3%	0.4%	2.7%	0.3%	0.2%	0.2%	2.9%	7.0%	0.0%	0.2%	1.0%	0.1%	6.5%	0.0%	0.2%	3.4%
6.4%	3.3%	9.0%	0.0%	0.5%	3.8%	2.4%	0.2%	0.0%	0.1%	4.3%	5.2%	0.6%	0.1%	0.8%	0.6%	4.3%	0.6%	0.7%	2.8%
10.4%	26.4%	2.9%	0.0%	0.5%	6.1%	6.6%	0.0%	0.0%	0.6%	2.8%	4.7%	0.6%	0.8%	1.0%	0.0%	1.2%	0.6%	0.6%	1.4%
4.3%	3.9%	17.3%	0.0%	1.1%	1.1%	0.4%	0.3%	0.1%	0.2%	2.9%	4.2%	0.7%	0.2%	1.2%	4.5%	3.9%	0.7%	0.0%	0.1%
4.9%	5.8%	7.4%	0.0%	0.7%	3.9%	3.2%	0.1%	0.1%	0.0%	2.9%	3.6%	0.8%	0.0%	0.9%	4.2%	3.3%	0.8%	0.9%	0.0%
4.2%	3.4%	8.3%	0.0%	4.0%	9.9%	3.2%	0.6%	0.6%	0.0%	1.6%	3.5%	0.9%	0.0%	1.3%	1.4%	2.8%	0.9%	0.0%	0.1%
4.1%	**8.0%**	**9.2%**	**0.0%**	**1.1%**	**4.1%**	**4.0%**	**0.2%**	**0.2%**	**0.2%**	**3.1%**	**5.0%**	**0.7%**	**0.2%**	**0.9%**	**2.1%**	**4.6%**	**0.7%**	**0.9%**	**1.3%**

The average deviation between the reconciled and measured values was less than 5% for all of the variables. The only major systematic deviation was observed in inlet CO_2 (4.6%), which caused an average change of 5.3% in rich loading. Similar results were obtained in independent analysis done on the same data for dynamic modeling of flash vessels (Walters et al., 2012) and absorber modeling (Sachde et al., Modeling Pilot Plant Performance of an Absorber with Aqueous Piperazine, 2012) which showed deviation of 4.7% and 7.5% for CO_2 concentration, respectively.

The major variables of interest were CO_2 stripped and heat duties of steam heaters. Figure 40 to Figure 44 shows the difference between the reconciled and measured value for these variables. Model predictions were in good agreement with measured values. There was an average systematic shift of +3.4% in heat duties of the HP heater and -3.3% in the LP heater. This deviation can be attributed to unequal distribution of heat losses to heaters which were subtracted from measured values of heat duties.

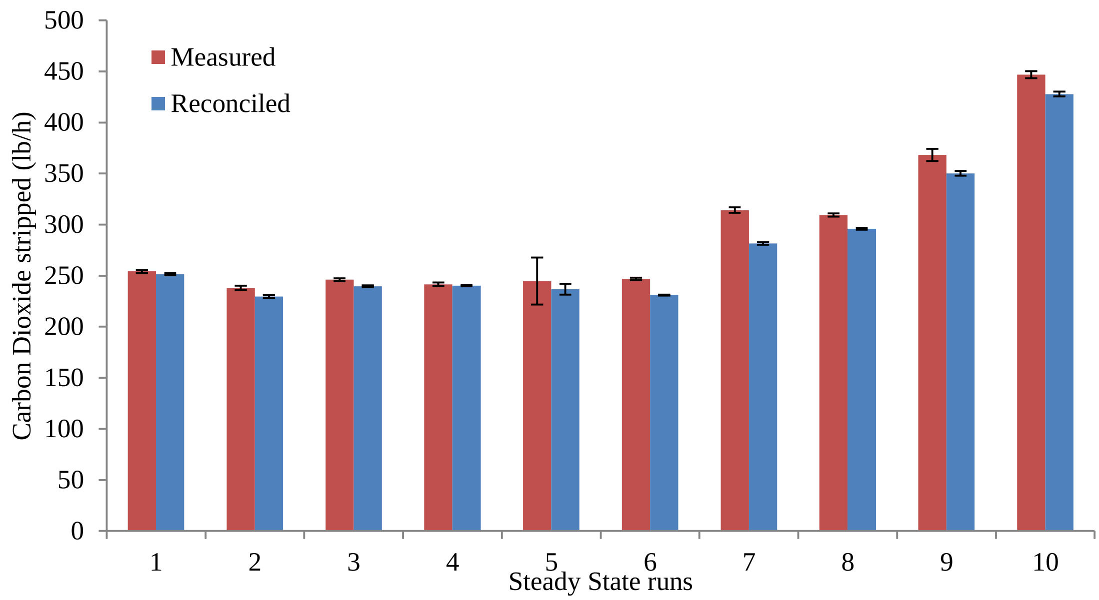

Figure 40: Difference between measured and reconciled values for carbon dioxide stripped in each steady state run (Fall 2011 campaign)

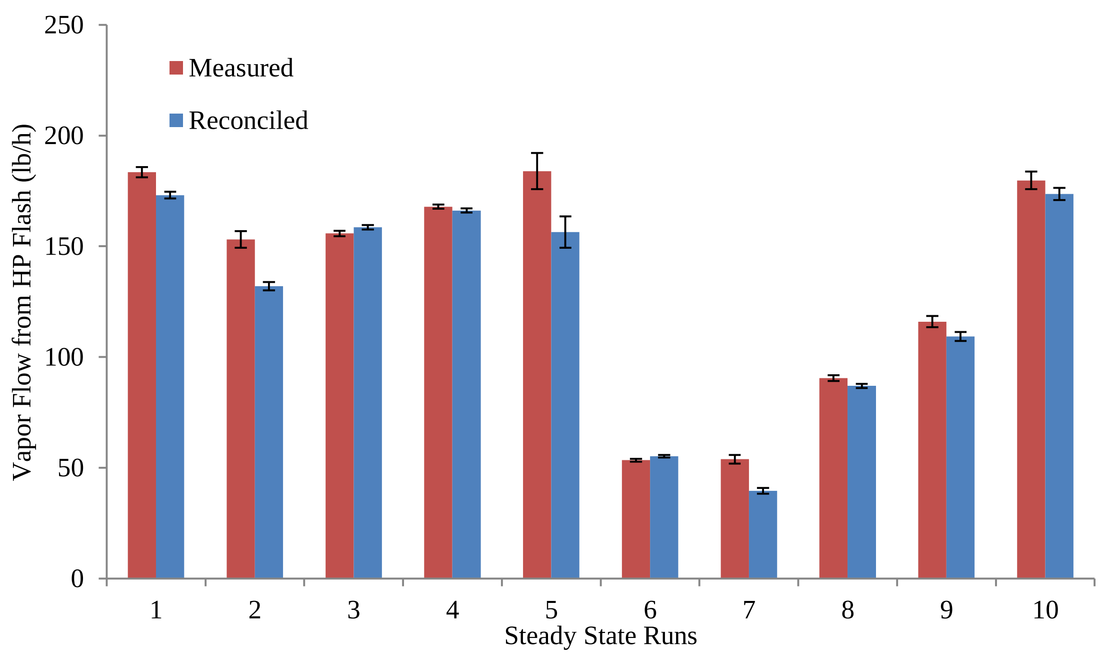

Figure 41: Difference between measured and reconciled values of HP flash vapor flow for each steady state run (Fall 2011 campaign)

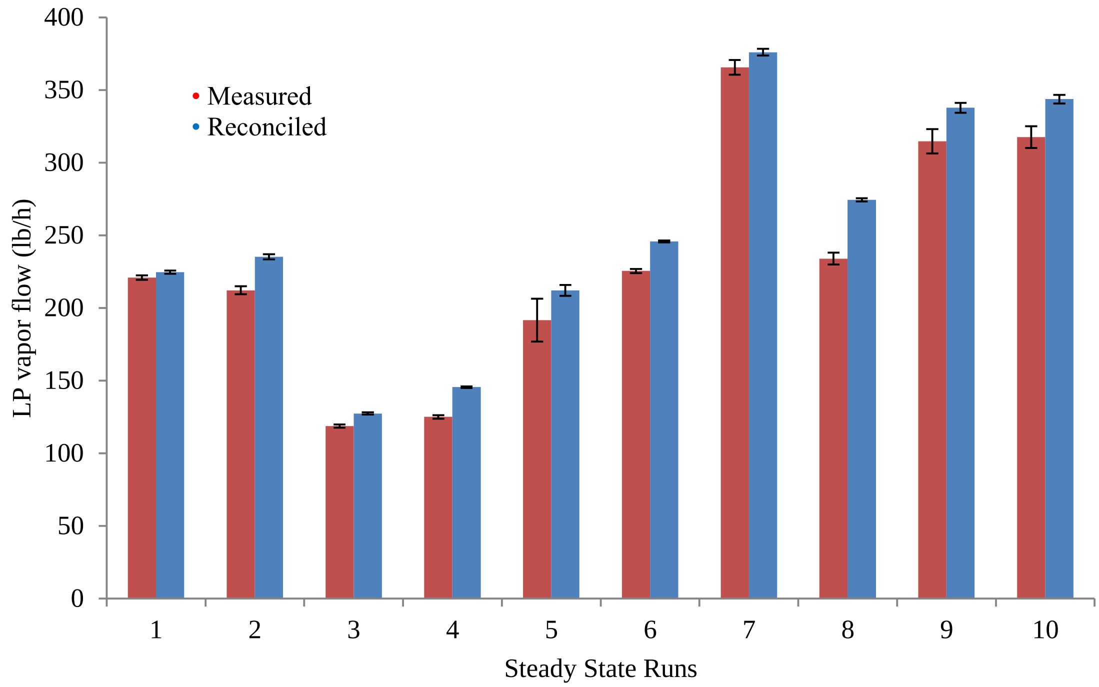

Figure 42: Difference between measured and reconciled values of LP flash vapor flow for each steady state run (Fall 2011 campaign)

Figure 43 and Figure 44 gives the difference between measured and reconciled values of HP and LP heater duties.

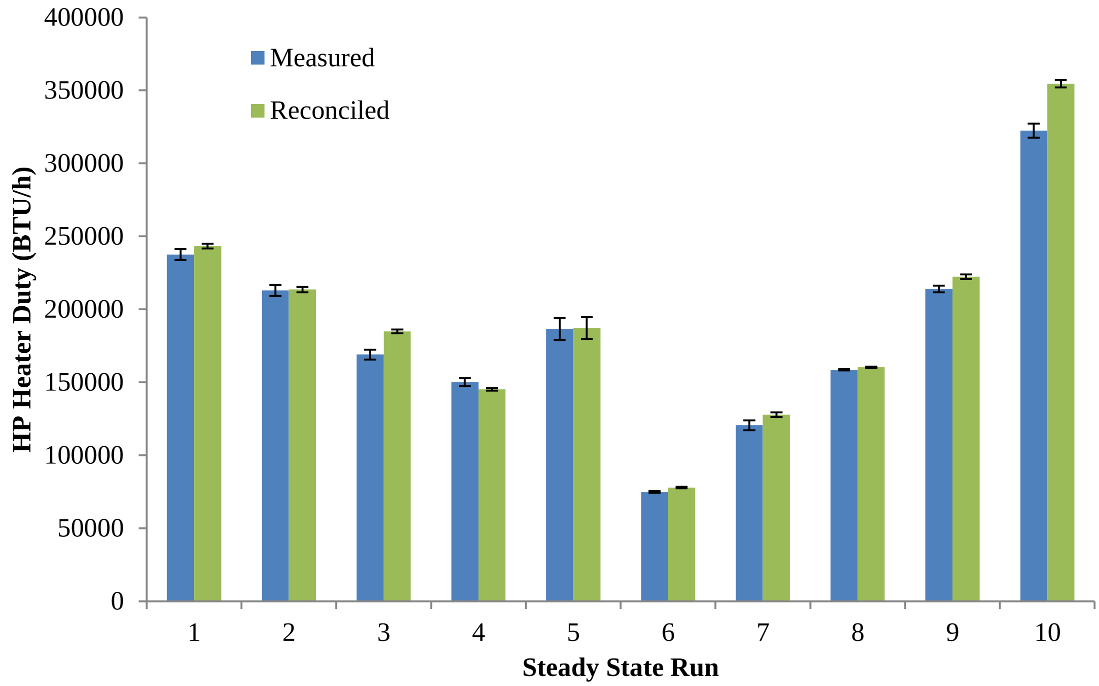

Figure 43: Difference between measured and reconciled values of HP heater duty flow for each steady state run (Fall 2011 campaign)

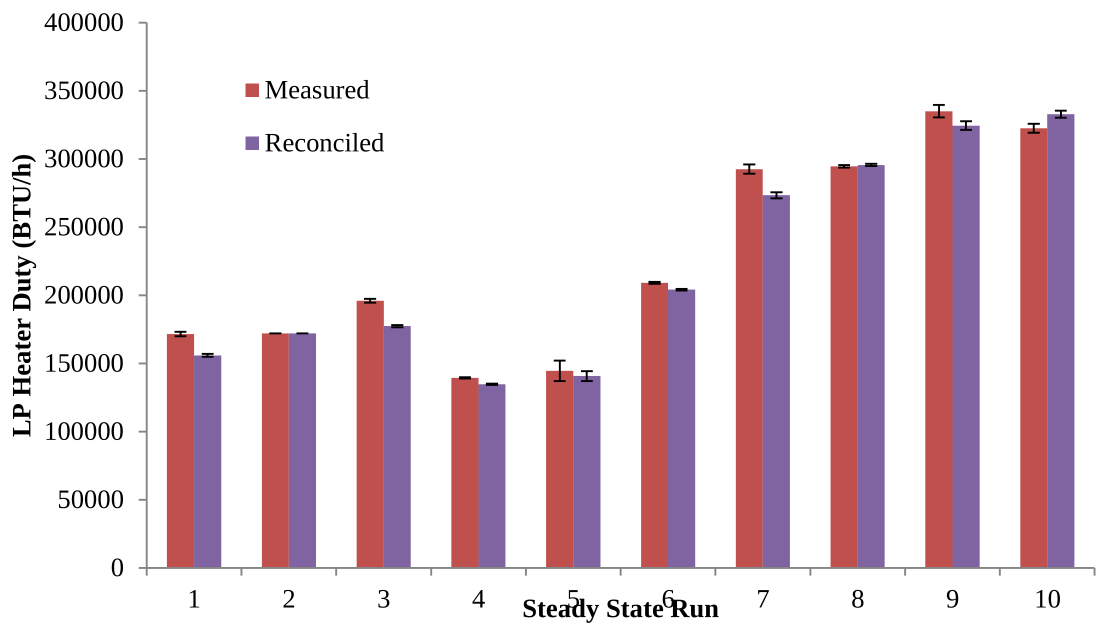

Figure 44: Difference between measured and reconciled values of LP heater duty flow for each steady state run (Fall 2011 campaign)

The major systematic deviation was in the rich and lean loading due to manipulation in inlet CO_2 done by Aspen Plus® for reconciliation. This deviation is shown in Figure 45.

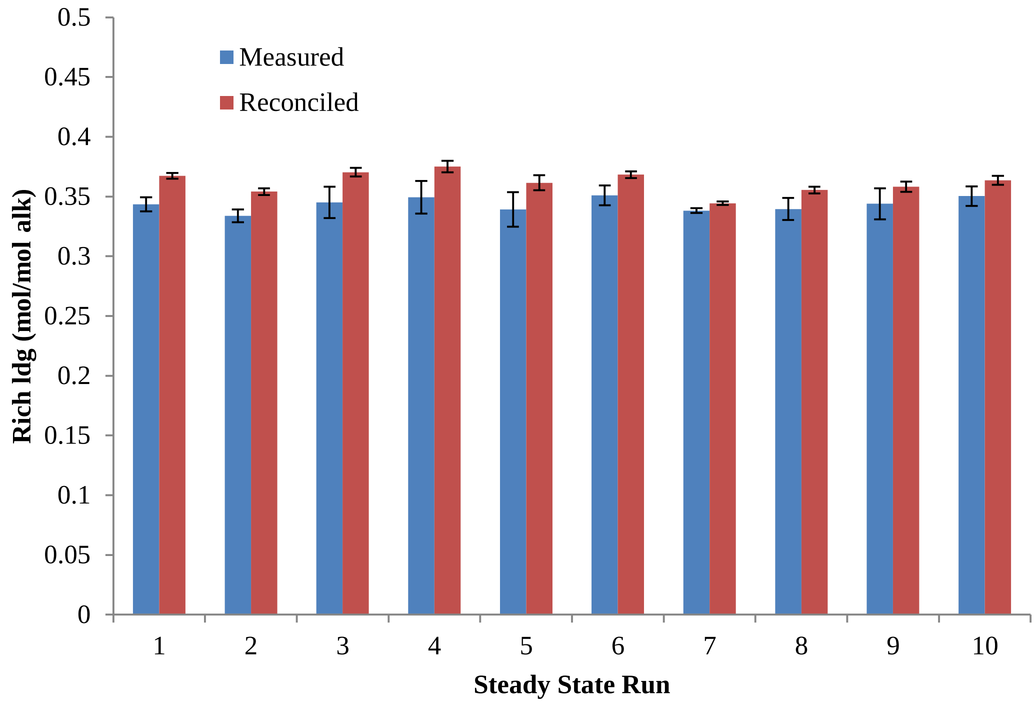

Figure 45: Difference between measured and reconciled values of rich loading for each steady state run (Fall 2011 campaign)

The error in rich loading propagated through to the lean loading as shown in Figure 46.

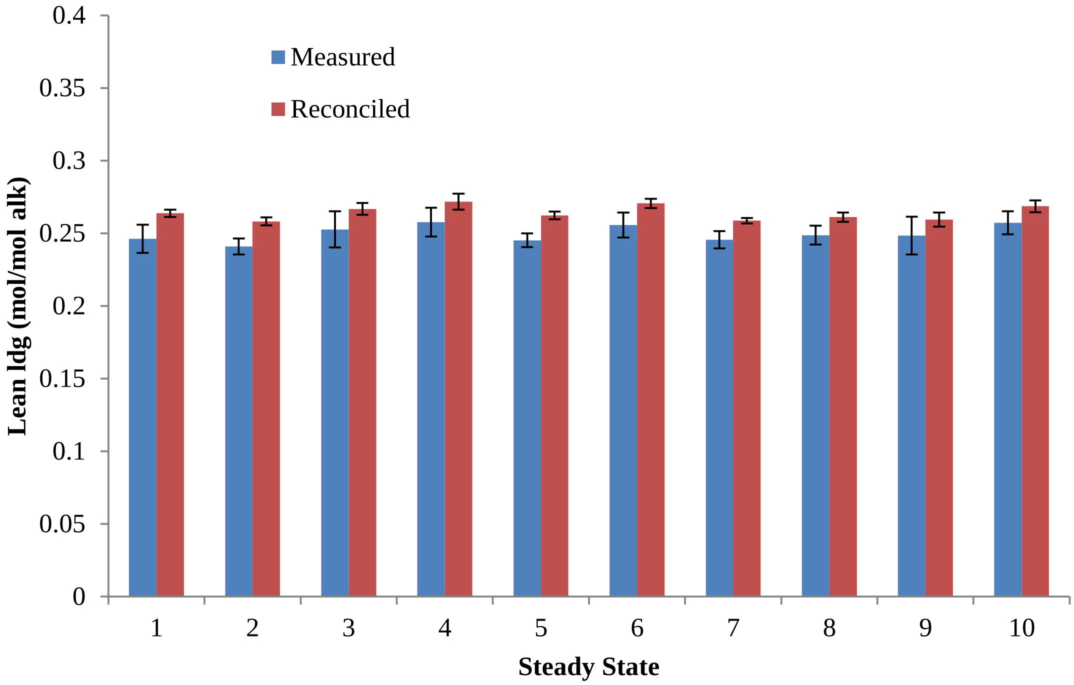

Figure 46: Difference between measured and reconciled values of lean loading for each steady state run (Fall 2011 campaign)

The deviation between measured and reconciled values of important variables is given in Table 34.

Table 34: Mean absolute error of important variables of Fall 2011 campaign, heater duty corrected for heat loss and overhead flow corrected for molecular weight

Parameter	Average absolute deviation between reconciled and measured value
Lean CO_2 flow	5.0%
Lean PZ flow	0.7%
Rich CO_2 flow	4.6%
Semirich CO_2 flow	3.1%
LP Flash T	0.9%
HP Flash T	0.2%

LP Flash P	1.0%
HP Flash P	0.0%
Stripped CO_2	4.1%
HP Overhead flow	8.0%
LP Overhead flow	9.2%
HP Heater Duty	4.0%
LP Heater Duty	4.0%
Cross Exchanger T	0.2%
Average	**2.5%**

The reconciliation process demonstrated the agreement of the model with actual pilot scale operation with minor correction required in CO_2 measurement. Reconciled values of pilot plant operation were used for analysis of energy performance and optimization.

4.3.4 Reconciliation errors and Recommendations

Although good reconciliation was achieved between measured and modeled values for most of the operating variables, the residual error between the two can be attributed to the following reasons.

- HP and LP Flow measurement errors – As mentioned above, there is already one adjustment of HP and LP vapor flow molecular weight done in the reconciliation. However, other errors were also found in the measurement by other works. Reconciliation on same set of data was done by other researchers for dynamic modeling (Walters M. , 2013) to understand off-design behavior and develop control strategies. That work focused on the gas flow measurement and its errors. It was identified that gas density and compressibility were set to manual input in these instruments resulting in the instruments ignoring actual temperature and pressure. Other errors included inconsistency of pressure measurement location, which was marked as upstream in measurement and downstream in calculator block of the instrument computer. There was one faulty unit conversion in the measurement block and parameter correction in calculation (Walters M. , 2013). However, final corrected values reported in the work were not significantly different than the ones used in this work. It is recommended to rectify these errors in future campaigns.

- HP and LP heat duty measurements – There was one adjustment build into reconciliation related to equal distribution of HP and LP steam loss as mentioned above, but other than that, errors were observed in the steam measurement instruments. These were same as errors mentioned in the above flow measurement instruments.
- Loading measurement – Several inconsistencies were reported in loading measurements operation. Auto titrator samples were analyzed in batches of 5 to 10 at a time, and concentration of MeOH declined due to evaporation, resulting in measurement errors. Sample collection of semi-rich sample is also prone to error due to high pressure resulting in some vapor loss when the sample is taken. This can explain higher error in initial steady state runs. It is recommended to do loading measurements in controlled laboratory environment and also inclusion of online loading measurement in future campaign.
- Solvent degradation – Same solvent was used in two campaigns which were approximately a year apart. Solvent degradation can be expected resulting in less than expected performance in winter campaign. The effect can partially

explain consistent under-prediction of pressure in the VLE curve of Figure 38 and Figure 39. It is recommended to use fresh solvent for future campaigns

- Approach to equilibrium – First stage flash was modeled as one equilibrium stage in Aspen Plus®, while the actual stage may not be in perfect equilibrium.
- Modeling of cold rich bypass – Cold rich bypass was modeled as Ratesep® block in Aspen Plus® with 1 m of packing. Due to lack of temperature and concentration measurement at different points in the packing, it is difficult to predict the actual behavior of packing, and hence modeling of the packing section may not represent actual behavior of LP flash. It is recommended to use additional instrument for performance measurement of stripper packing section, especially when Advanced Flash configuration is used in the next campaign.

4.4 PILOT PLANT ENERGY PERFORMANCE

4.4.1 Equivalent Work

Equivalent Work as described in Chapter 2 and given in Equation 7 was used to quantify the performance of pilot plant during the campaign.

$$W(eq) = 0.75\left(\frac{T_{reb} + \Delta T - T_{sink}}{T_{reb} + \Delta T}\right)Q_{reb} + W_{pump} + W_{comp}$$

Equation 7: Equivalent Work equation used for calculating equivalent energy requirement of pilot plant campaign runs

4.4.2 Results

Table 35 shows the equivalent work for the winter campaign. Expected heat loss based on Equation 6 was subtracted from measured value of reboiler duty. For the equivalent work calculations, a temperature approach of 5°C between steam and heater was used, with an assumed sink temperature of 40°C.

Table 35: Equivalent Work for all steady state runs of Winter 2011 campaign

Run	Q_{reb} kJ/mol CO_2	W_{eq} kJ/mol CO_2
1	225.8	55.02
2	178.2	45.80
3	217.0	53.34
4	184.7	47.69
5	261.9	62.08
6	279.1	65.24
7	188.7	46.72
8	**170.3**	**45.45**

Reconciled values of heat duties were used to determine the equivalent work for the Fall campaign given in Table 36.

Table 36: Equivalent Work for all steady state runs of Fall 2011 campaign, compression work based on Van Wagener correlations and pump work calculated in Aspen Plus® for each run on

Run	Q_{reb} kJ/mol CO_2	W_{reb} kJ/mol CO_2	W_{comp} + W_{pump} kJ/mol CO_2	W_{eq} kJ/mol CO_2
1	160.5	32.3	10.9	43.2
2	169.7	34.2	11.0	45.2
3	154.1	31.0	10.7	41.9
4	118.6	23.9	10.9	36.6
5	140.2	28.2	11.0	41.2
6	124.2	25.0	11.1	38.8
7	144.6	29.1	11.3	43.8
8	157.1	31.6	10.9	43.2
9	159.1	32.0	10.9	43.7
10	163.9	33.0	10.4	44.6

The Fall campaign showed significant improvement due to more optimal operating conditions, use of cold rich bypass, and better heat recovery in cross exchangers. The validated model was used to further optimize the energy performance of the pilot plant configuration.

4.5 Process Modeling And Simulation

4.5.1 Sensitivity Analysis on Rich Loading

One of the important variables responsible for better energy performance of any stripper configuration is rich loading. A validated model of the pilot plant was used to determine the achievable values of equivalent work for different rich loading. The best energy performance achieved in the pilot plant was an equivalent work of 36.6 kJ/mol CO_2 with 0.375 rich loading (Run 4). Table 37 shows the value of energy performance of pilot plant configuration for different values of rich loading. Other variables which can affect the energy performance of the system were kept the same as Run 4 to isolate the effect of rich loading on energy performance. These values were 0.272 lean loading, bypass flow as 10% of total flow at 104 °C, and pressure ratio of 1.5.

Table 37: Sensitivity analysis of rich loading on pilot plant configuration. 8m PZ, Fawkes model, 5 C LMTD Cross exchanger, 150 C regeneration T, 1.5 HP/LP Pressure Ratio

Rich loading mol/mol alk	Equivalent Work kJ/mol CO_2
0.35	39.3
0.36	38.1
0.37	37.0
0.38	36.1
0.39	35.4
0.40	**34.6**

The practical maximum value of rich loading that can be achieved with an expanded, intercooled absorber is 0.4. It should translate to an improvement of 5.3% over the best value achieved in these pilot plant campaigns.

4.5.2 Sensitivity Analysis on Pressure Ratio

The pressure ratio of the two flash vessels will mainly be governed by the pressure ratio of the first CO_2 compressor stage. Since CO_2 is recovered at two pressure stages, the CO_2 from the LP flash will be compressed to the pressure of CO_2 recovered from the HP flash in the first compressor stage. Typically, one compressor stage has a compression ratio of 1.5 to 2. A sensitivity analysis on pressure ratio was done on operating conditions of Run 4 to determine the optimum value of pressure ratio. Results are shown in Table 38.

Table 38: Sensitivity analysis of HP/LP Pressure ratio on pilot plant configuration. 8m PZ, Fawkes model, 5 C LMTD Cross exchanger, 150 C regeneration T, 0.38 rich loading

Pressure Ratio	**Equivalent Work** kJ/mol CO_2
1.25	36.6
1.5	**36.1**
1.75	36.7
2	37.4

A pressure ratio of 1.5 was found to be optimum and was used for process optimization of lean loading and cold rich bypass flow. There is a slight difference in the modeled and achieved performance at pressure ratio 1.5 due to the difference in cross exchanger specification which was 5°C LMTD in the model, while actual performance achieved was slightly different. There was an improvement of 3.5% over performance at pressure ratio 2.

4.5.3 Process optimization

Other variables in the process that can be optimized for energy performance are:

- Lean loading,
- Cold rich bypass flow,
- Cross Exchanger area/LMTD specification

The validated process model was used to optimize these conditions to identify best energy performance achievable in the pilot plant configuration. Analysis was done for two values of rich loading, 0.375 (achieved in pilot plant) and 0.4 (possible with an upgraded absorber). Sensitivity analysis was done on the above variables to determine the optimum equivalent work. An LMTD specification of 5 °C on both cross exchangers was used for all the cases as a practical design specification. When both cross exchangers in the pilot plant were used, the combined heat exchanger area was able to achieve better heat recovery than a heat exchanger area designed for 5°C LMTD. However, the over-designed case of the pilot plant heat exchanger was ignored and a 5°C LMTD specification was used as a practical design on commercial units. A pressure ratio of 1.5 was used, as determined in previous analysis.

Figure 47 shows equivalent work for different values of lean loading. For each value of lean loading, the cold rich bypass flow was optimized.

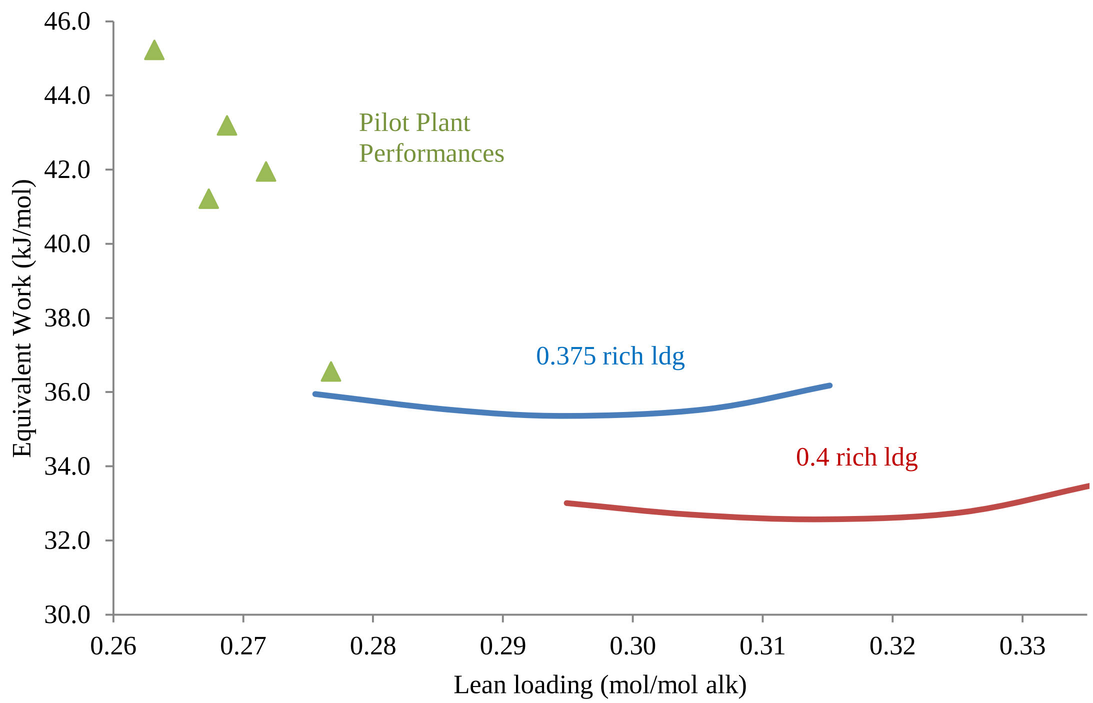

Figure 47: Lean loading optimization of pilot plant configuration (5 C LMTD Cross exchanger) and comparison with actual pilot plant performances of Fall 2011 campaign

Optimum values of 35.4 kJ/mol and 32.6 kJ/mol were achieved for 0.375 (at 0.29 lean loading and 6% bypass flow) and 0.4 (at 0.31 lean loading and 4% bypass flow) rich loading respectively. This is an improvement of 3% and 11% over the best value achieved in the pilot plant.

The benefit of cold rich bypass was also analyzed by comparing energy performance of the two-stage flash without cold rich bypass. Additionally, the benefit of cold rich bypass to HP flash was analyzed by comparing performance of the configuration with bypass flows to both HP and LP flash. Figure 48 compares equivalent work values of these three configurations over a range of lean loading.

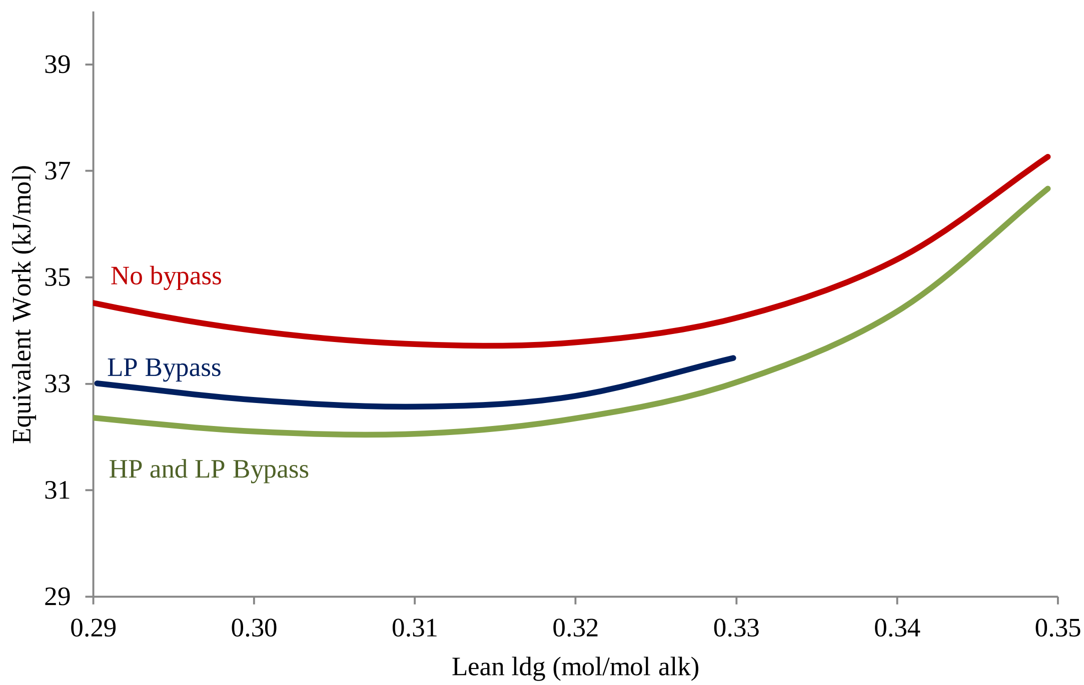

Figure 48: Equivalent work for different configurations over a range of lean loading. 8 m PZ solvent, 150 °C stripping T, optimized cold rich bypass flow, 5 °C LMTD Cross Exchanger, 0.4 rich loading

There was an improvement of 3.5% from the case of no bypass and an additional improvement of 1.5% is achievable by implementing bypass on the HP flash.

4.6 Conclusions

1. The Fawkes model represents PZ-CO_2-H_2O fairly accurately. The model accurately represented the actual performance in the pilot plant.
2. An average correction of 4.6% was required in CO_2 flow for data reconciliation using the Fawkes model, which can be attributed to systematic measurement errors in titration. Observed errors in these measurements were found to propagate to approximately 5–10% in total pressure measurement equation which describes the minor differences observed between the reconciled and measured values.
3. No other major systematic deviations were observed in any other measurements, including heat duties and CO_2 stripped, which reconciled to within 4% deviation.
4. The best energy performance of 36.6 kJ/mol CO_2 in the Fall campaign.
5. Better energy performance is predicted at the higher rich loadings of 0.4 theoretically achievable by piperazine.
6. The optimized validated model achieved equivalent work of 32.6 kJ/mol CO_2 by optimizing operating conditions. Optimum operating conditions were found to be 0.31 lean loading and 4% cold rich bypass at 0.4 rich loading.

Chapter 5: Stripper Modeling for Carbon Capture in Natural Gas Combustion

This chapter describes the stripper modeling for CO_2 removal from natural gas combustion using amine scrubbing with 8 m piperazine as solvent. This work was sponsored by TOTAL (through the Process Science and Technology Center) for development of heat and material balances for multiple cases of absorption of CO_2 from natural gas combustion flue gas using aqueous piperazine.

5.1 Natural Gas Combustion

CO_2 capture from natural gas is becoming important as combustion of natural gas for electricity generation is getting popular due to abundance of natural gas in United States. Natural gas burns cleaner than coal, resulting in lesser emissions than burning of coal.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Flue gases from three cases were considered for the work.

5.1.1 Combined Cycle Gas Turbine

The combined cycle is a combination of two thermodynamic cycles as seen in Figure 49 (Engineering Design Encyclopedia). Natural gas is used to operate a gas turbine, resulting in hot exhaust which powers a steam cycle.

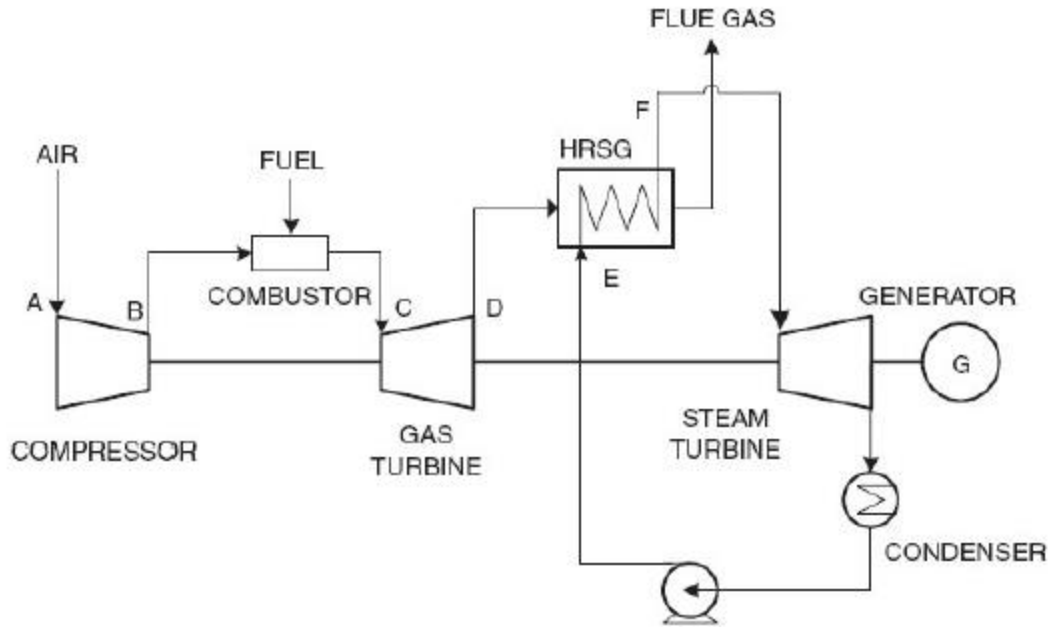

Figure 49: Schematic of operation of combined cycle

5.1.2 Combined Gas Turbine with Exhaust Gas Recycle (EGR)

EGR results in an increase in CO_2 concentration in the flue gas. Portion of the exhaust gas is recycled into the air inlet replacing nitrogen in the air creating a CO_2 rich exhaust.

5.1.3 Natural Gas Fired Boiler

The Natural Gas Boiler burns natural gas to create heat used for creating steam from water.

Table 39 shows the flue gas concentration used for the modeling and simulation of solvent regeneration for all three cases. Major differences are in CO_2 concentration which are approximately 3%, 6% and 9% respectively for the three cases and water concentration.

Table 39: Flue Gas conditions

Flow rate (kmol/h)	40 473	24 172	10 292
Flow rate (t/h)	1 161	691	284
Temperature (°C)	121	121	136
Pressure (kPag)	0	0	0
Molar Composition (%)			
H_2O	6.51	7.06	18.78
CO_2	3.31	6.18	8.69
N2	75.48	78.94	69.92
Ar	0.91	0.95	0.89
O_2	13.79	6.87	1.72
He (ppmv)	15	15	25
CO (ppmv)	50	50	380
NO_x (ppmv) – NO_2/NO_x	30	30	450
Particles & unburned HC (kg/h)	15	15	10

5.2 METHODOLOGY

Stripper modeling for the natural gas combustion cases was done using the Fawkes Model for piperazine in Aspen Plus®. Absorber modeling was done separately by Darshan Sachde with two cases with and without the Direct Contact Cooler (DCC) for each flue gas. The absorber modeling resulted in a set of lean and rich loading for each case which was used as an input to stripper modeling. These values are given in Table 40.

Table 40: Rich and lean loading values based on absorber modeling for all simulated cases of natural gas combustion

		DCC		No DCC	
		Rich ldg	Lean ldg	Rich ldg	Lean ldg
3% CO_2	Low capex	0.343	0.25	0.34	0.25
	High capex	0.358	0.25	0.355	0.25
6% CO_2	Low capex	0.358	0.25	0.360	0.25
	High capex	0.376	0.25	0.378	0.25
9% CO_2	Low capex	0.371	0.27	-	-
	High capex	0.391	0.27	-	-

The main objective of the work was to quantify the energy requirement (equivalent work) for each case and develop a set of heat and material balances. Additionally, sensitivity analysis on operating conditions, development of equipment tables, and optimization of major operating variables was done for all the cases.

Two cases corresponding to low capex (high opex) and high capex (low opex) were identified and simulated for each set of operating conditions.

5.2.1 Process Configurations

For this work, two process configurations were identified as low capex and high capex configurations. Selection of these configurations was based on previous results of stripper modeling as detailed in Chapter 3 and discussions with TOTAL. Quantification of actual capex and opex was not in the scope of this work but relative difference between capex of two configurations was established based on complexity and number of equipment items in each configuration. Similarly, opex was not quantified but the difference is indicated by value of equivalent work which was calculated for each operating case.

5.2.1.1 Low Capex Case

From the stripper modeling perspective, the configuration of simple stripper with cold rich bypass was selected as the low capex case. It is a minor modification over the conventional case of simple stripper which is expected to be a low cost modification because it does not require any new equipment. The configuration is shown in Figure 50.

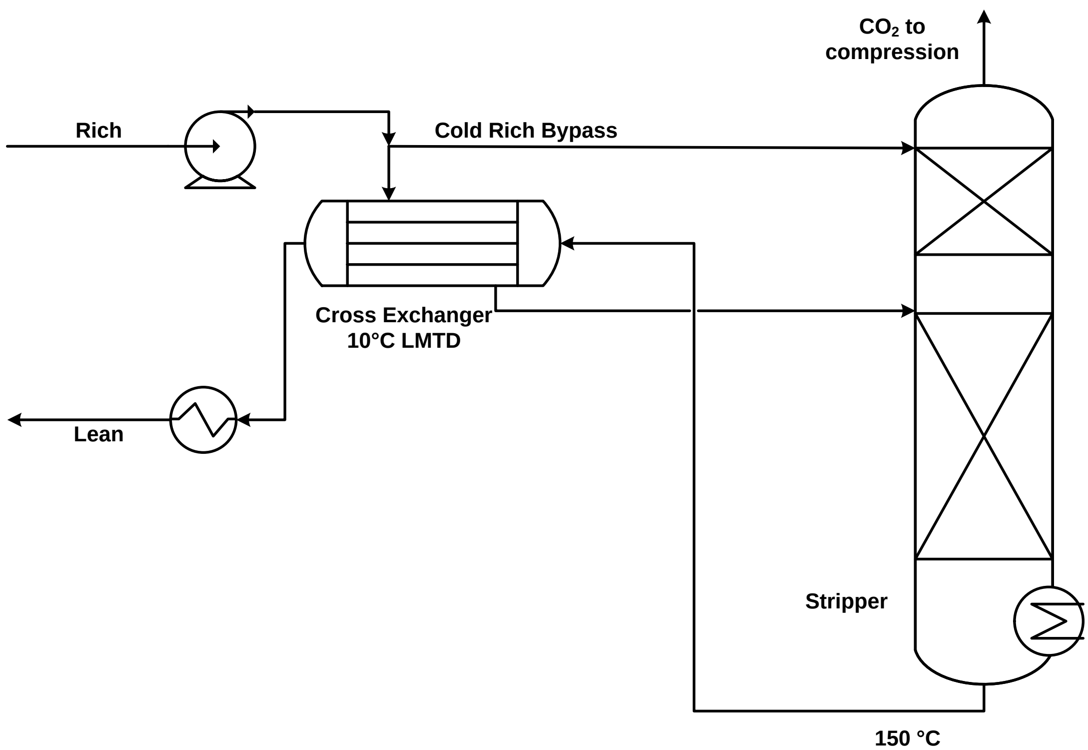

Figure 50: Low capex configuration of simple stripper with cold rich bypass (8m PZ, Mellapak 250X packing, 10C cross exchanger LMTD)

In this configuration, a small fraction of cold rich solvent is bypassed from the main cross exchanger and is sent directly on top of the stripper where it contacts with the hot CO_2/H_2O vapor coming from the hot solvent. This contact leads to heat recovery as most of the water vapor is condensed by the cold solvent in this section. This modification has proved to be an effective method of heat recovery as shown in Chapter 2 and Chapter 4.

Major highlights of this configuration are as follows

1. Cross Exchanger design – 10°C LMTD (As compared to typical design specification of 5°C used in most other simulations of this work, a 10°C specification implies a smaller cross exchanger area resulting in low capex)
2. Solvent rate – 1.4 L_{min} (As compared to typical design specification of 1.2 L_{min}, 1.4 corresponds to lesser packing requirement with a tradeoff of more solvent requirement)

Equivalent work, defined in Chapter 2 was calculated for each case.

5.2.1.2 High Capex Case

Stripper configuration of interheated stripper was used for this scenario, as shown in Figure 51. The configuration has already proven to be more efficient than conventional stripper configuration for coal combustion cases with respect to equivalent work as shown in Chapter 2, but is expected to have a higher capex due to an additional cross exchanger and a need for a high temperature pump.

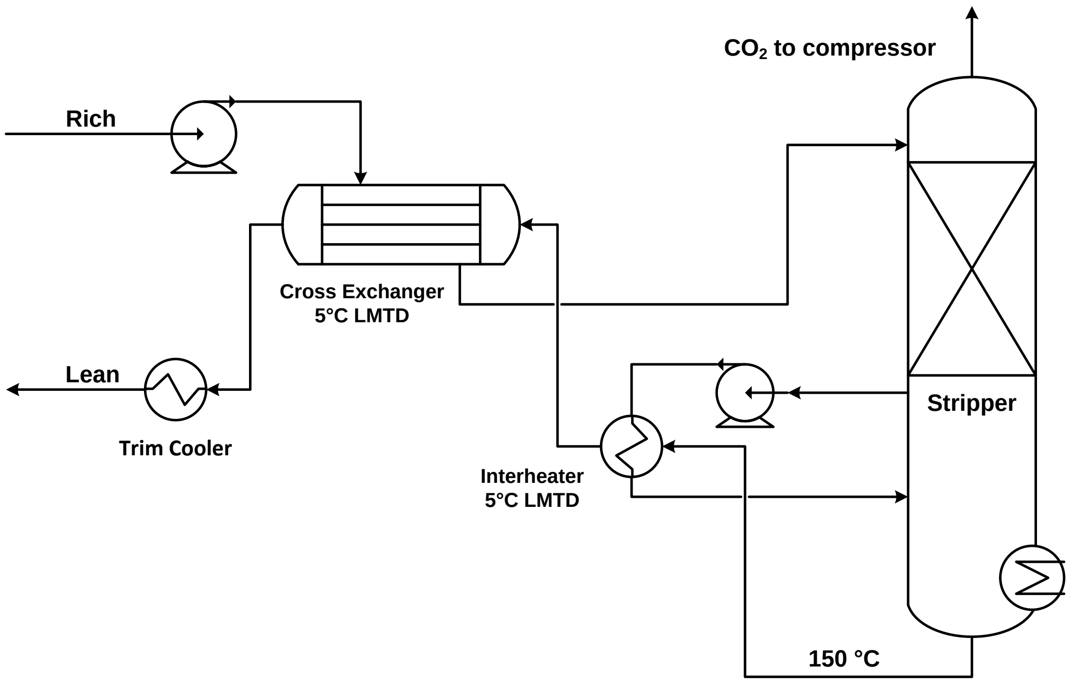

Figure 51: High capex configuration of interheated stripper. 8m PZ, 5C LMTD cross exchanger

In this configuration, heat is recovered from the hot lean solvent from the stripper bottom in two stages, first by the semi-heated solvent from the bottom of the top section of the stripper and then by the main cold feed to the stripper. Heat recovery in two stages results in reversible heat transfer and lower temperatures on stripper top. As a result, most of the water vapor is condensed within the top section of the stripper helping in reducing the overall energy requirement.

Major highlights of the configuration are as follows

1. Cross exchanger design – 5°C LMTD, both exchangers flashing (Will result in better heat recovery with associated higher capex in cross exchanger)
2. Solvent rate – 1.2 L_{min} (Will result in more packing requirement but lesser amount of solvent)

3. Packing – 5m Mellapak 250X was used for packing to simulate the top section above the interheater. Stage below the interheater was simulated as 1 equilibrium stage.

Equivalent Work was calculated for each simulation.

5.2.2 Simulation Parameters

Other modeling parameters which were same in both the configurations were as follows.

1. 8m piperazine as solvent, Fawkes model
2. 150°C reboiler temperature, based on 155°C steam availability as mentioned by TOTAL
3. Final discharge pressure of 150 bar. Correlations developed previously (Van Wagener, 2011) were used for calculation of compression work.

5.3 RESULTS

2 cases (DCC and no-DCC) were simulated (Sachde, Absorber Modeling for carbon capture from Natural Gas Combustion, 2013) for the absorber at each flue gas condition. This resulted in a set of lean and rich loading. These are given in Table 4. Although cases with DCC will require additional capital cost, actual capital cost estimation was not done and both the cases of DCC and no DCC were evaluated with low and high capex configurations.

Table 41 to Table 46 show the important results for these particular cases simulated for the work.

5.3.1 Combined Cycle

5.3.1.1 Low Capex Case

Table 41: Equivalent Work and other important results for combined cycle flue gas low capex case (Simple stripper with cold rich bypass, 3% CO_2, 8m PZ, 10°C LMTD cross exchanger, 150°C reboiler)

	DCC	**No DCC**
Rich loading (mol/mol alk)	0.343	0.34
Lean loading (mol/mol alk)	0.25	0.25
Reboiler Duty (kJ/mol CO_2)	145.0	146.9
Reboiler Equivalent Work (kJ/mol CO_2)	29.2	29.6
Electric Work, pumps and compressors (kJ/mol CO_2)	11.3	11.3
Total Equivalent Work (kJ/mol CO_2)	**40.5**[5]	**40.9**[6]

Best performance of 3% case or combined cycle case was 40.5 kJ/mol which is approximately 18% more than equivalent work of corresponding configuration for coal (12% CO_2).

5.3.1.2 High Capex Case

Table 42: Equivalent Work and other important results for combined cycle flue gas high capex case (Interheated Stripper, 3% CO2, 8m PZ, 5°C LMTD cross exchanger, 150°C reboiler)

	DCC	**No DCC**
Rich loading (mol/mol alk)	0.358	0.355
Lean loading (mol/mol alk)	0.25	0.25
Reboiler Duty (kJ/mol CO_2)	117.6	119.1

[5] Optimum bypass of 6%

[6] Optimum bypass of 6%

Reboiler Equivalent Work (kJ/mol CO_2)	23.7	24.0
Electric Work, pumps and compressors (kJ/mol CO_2)	11.2	11.2
Total Equivalent Work (kJ/mol CO_2)	34.9	35.2

The best total equivalent work of 34.9 kJ/mol CO_2 is approximately 12% worse than equivalent performance of coal combustion.

5.3.2 Combined Cycle with EGR

5.3.2.1 Low Capex Case

Table 43: Equivalent Work and other important results for combined cycle flue gas with EGR, low capex case (Simple stripper with cold rich bypass, 6% CO2, 8m PZ, 10°C LMTD cross exchanger, 150°C reboiler)

	DCC	**No DCC**
Rich loading (mol/mol alk)	0.358	0.360
Lean loading (mol/mol alk)	0.25	0.25
Reboiler Duty (kJ/mol CO_2)	136.0	135.0
Reboiler Equivalent Work (kJ/mol CO_2)	27.4	27.2
Electric Work, pumps and compressors (kJ/mol CO_2)	11.1	11.1
Total Equivalent Work (kJ/mol CO_2)	38.5[7]	38.3[8]

5.3.2.2 High Capex Case

Table 44: Equivalent Work and other important results for combined cycle flue gas with EGR, high capex case (Interheated Stripper, 6% CO2, 8m PZ, 5°C LMTD cross exchanger, 150°C reboiler)

	DCC	**No DCC**
Rich loading (mol/mol alk)	0.376	0.378

[7] Optimum bypass of 8%

[8] Optimum bypass of 8%

Lean loading (mol/mol alk)	0.25	0.25
Reboiler Duty (kJ/mol CO_2)	110.2	109.7
Reboiler Equivalent Work (kJ/mol CO_2)	22.2	22.1
Electric Work, pumps and compressors (kJ/mol CO_2)	11.1	11.0
Total Equivalent Work (kJ/mol CO_2)	33.3	33.1

5.3.3 Natural Gas Boiler

5.3.3.1 Low Capex Case

Table 45: Equivalent Work and other important results for natural gas boiler, low capex case (Simple stripper with cold rich bypass, 9% CO2, 8m PZ, 10°C LMTD cross exchanger, 150°C reboiler)

	DCC
Rich loading (mol/mol alk)	0.371
Lean loading (mol/mol alk)	0.27
Reboiler Duty (kJ/mol CO_2)	132.0
Reboiler Equivalent Work (kJ/mol CO_2)	26.6
Electric Work, pumps and compressors (kJ/mol CO_2)	10.9
Total Equivalent Work (kJ/mol CO_2)	37.5[9]

5.3.3.2 High Capex Case

Table 46: Equivalent Work and other important results for natural gas boiler case, high capex (Interheated Stripper, 9% CO2, 8m PZ, 5°C LMTD cross exchanger, 150°C reboiler)

	DCC
Rich loading (mol/mol alk)	0.391

[9] Optimum bypass of 6%

Lean loading (mol/mol alk)	0.27
Reboiler Duty (kJ/mol CO_2)	103.7
Reboiler Equivalent Work (kJ/mol CO_2)	20.9
Electric Work, pumps and compressors (kJ/mol CO_2)	10.7
Total Equivalent Work (kJ/mol CO_2)	31.6

This case had the best performance of 31.6 kJ/mol due to highest concentration of CO_2 in flue gas resulting in rich loading values almost same as that of coal.

5.3.4 Rich Loading Sensitivity Analysis

For high capex case of interheated stripper, a sensitivity analysis on rich loading was done to identify the relation between rich loading and equivalent work. Further, lean loading was also varied to identify an optimum value of lean loading for each case of rich loading. Major specifications were

1. 8m PZ, Fawkes model, 150°C reboiler T, 150 bar compressor discharge P
2. 5°C LMTD Cross exchanger,
3. Variable lean loading, variable bypass flow

Error! Reference source not found. shows the value of equivalent work and ther important operating variables for all the rich loading cases simulated. For very low values of lean loading, there may be a possibility of solvent precipitation; however the solvent limitations were ignored for this work.

Table 47: Sensitivity Analysis on equivalent work for various values of rich loading (Interheated stripper high capex case, 5C LMTD cross exchanger and interheater, 150C stripper, 8m PZ, Fawkes model)

Rich loading = 0.28 mol/mol alk				
Lean loading	Reboiler Duty	Reboiler Equivalent Work	Compression Work	Total Equivalent Work

mol/mol alk	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2
0.15	176.3	35.52	11.60	47.58
0.16	173.0	34.86	11.52	46.89
0.17	170.2	34.28	11.44	46.29
0.18	168.2	33.89	11.35	45.89
0.19	167.2	33.69	11.26	45.67
0.20	**167.1**	**33.67**	**11.14**	**45.66**
0.21	168.4	33.91	11.02	45.94
0.22	171.3	34.52	10.88	46.61
0.23	176.9	35.64	10.73	47.89
0.24	186.0	37.46	10.57	49.98

Rich loading = 0.29 mol/mol alk				
Lean loading	Reboiler Duty	Reboiler Equivalent Work	Compression Work	Total Equivalent Work
mol/mol alk	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2
0.16	167.1	33.66	11.52	45.65
0.17	164.1	33.07	11.44	45.04
0.18	161.6	32.55	11.35	44.49
0.19	160.2	32.27	11.26	44.18
0.20	**159.1**	**32.05**	**11.14**	**43.95**
0.21	159.2	32.07	11.02	43.97
0.22	160.1	32.25	10.90	44.17
0.23	163.5	32.93	10.73	44.92
0.24	168.8	34.00	10.57	46.13

0.25	178.4	35.93	10.38	48.36

Rich loading = 0.30 mol/mol alk				
Lean loading	Reboiler Duty	Reboiler Equivalent Work	Compression Work	Total Equivalent Work
mol/mol alk	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2
0.17	158.3	31.89	11.44	43.82
0.18	155.7	31.37	11.36	43.27
0.19	153.4	30.90	11.25	42.75
0.20	152.1	30.64	11.15	42.47
0.21	151.4	30.50	11.03	42.31
0.22	**150.8**	**30.39**	**10.90**	**42.18**
0.23	153.4	30.90	10.73	42.71
0.24	156.2	31.47	10.57	43.34
0.25	162.3	32.68	10.37	44.73
0.26	171.4	34.53	10.17	46.87

Rich loading = 0.31 mol/mol alk				
Lean loading	Reboiler Duty	Reboiler Equivalent Work	Compression Work	Total Equivalent Work
mol/mol alk	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2
0.18	150.1	30.24	11.36	42.09
0.19	148.0	29.83	11.27	41.64
0.20	146.0	29.41	11.14	41.17
0.21	145.0	29.21	11.02	40.93

0.22	**144.4**	**29.10**	**10.88**	**40.79**
0.23	145.2	29.26	10.74	40.93
0.24	146.8	29.58	10.57	41.27
0.25	150.2	30.26	10.37	42.01
0.26	155.2	31.27	10.17	43.17
0.27	164.3	33.10	9.96	45.30

Rich loading = 0.32 mol/mol alk				
Lean loading	Reboiler Duty	Reboiler Equivalent Work	Compression Work	Total Equivalent Work
mol/mol alk	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2
0.19	142.4	28.69	11.26	40.45
0.20	140.9	28.38	11.15	40.10
0.21	139.4	28.08	11.03	39.75
0.22	**137.7**	**27.74**	**10.90**	**39.36**
0.23	138.2	27.84	10.74	39.41
0.24	138.9	27.97	10.56	39.52
0.25	140.5	28.30	10.38	39.86
0.26	143.8	28.97	10.18	40.59
0.27	149.9	30.20	9.93	42.00
0.28	159.3	32.09	9.68	44.24

Rich loading = 0.33 mol/mol alk				
Lean loading	Reboiler Duty	Reboiler Equivalent Work	Compression Work	Total Equivalent Work

mol/mol alk	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2
0.20	135.2	27.24	11.15	38.91
0.21	134.0	26.99	11.02	38.60
0.22	132.5	26.69	10.90	38.24
0.23	132.3	26.64	10.73	38.13
0.24	**132.2**	**26.64**	**10.58**	**38.08**
0.25	132.8	26.76	10.39	38.17
0.26	135.2	27.24	10.16	38.65
0.27	138.3	27.87	9.95	39.34
0.28	143.9	28.99	9.70	40.63
0.29	153.4	30.90	9.41	42.93

Rich loading = 0.34 mol/mol alk				
Lean loading	Reboiler Duty	Reboiler Equivalent Work	Compression Work	Total Equivalent Work
mol/mol alk	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2
0.21	129.2	26.02	11.04	37.59
0.22	127.7	25.73	10.90	37.23
0.23	127.1	25.60	10.75	37.03
0.24	126.7	25.52	10.57	36.88
0.25	**126.7**	**25.52**	**10.39**	**36.82**
0.26	127.6	25.71	10.17	36.97
0.27	129.5	26.10	9.95	37.35
0.28	133.0	26.80	9.70	38.12
0.29	139.3	28.05	9.40	39.57

0.30	149.2	30.06	9.09	42.03

Rich loading = 0.35 mol/mol alk				
Lean loading	Reboiler Duty	Reboiler Equivalent Work	Compression Work	Total Equivalent Work
mol/mol alk	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2
0.22	123.4	24.87	10.89	36.32
0.23	122.6	24.70	10.73	36.07
0.24	121.8	24.54	10.58	35.83
0.25	**121.4**	**24.46**	**10.38**	**35.67**
0.26	121.8	24.54	10.18	35.68
0.27	122.8	24.74	9.94	35.84
0.28	124.6	25.11	9.70	36.19
0.29	128.8	25.95	9.40	37.12
0.30	134.9	27.18	9.09	38.57
0.31	143.7	28.94	8.79	40.78

Rich loading = 0.36 mol/mol alk				
Lean loading	Reboiler Duty	Reboiler Equivalent Work	Compression Work	Total Equivalent Work
mol/mol alk	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2	kJ/mol CO_2
0.23	118.2	23.82	10.75	35.14
0.24	117.6	23.70	10.58	34.93
0.25	116.9	23.55	10.37	34.68
0.26	116.7	23.51	10.17	34.55

0.27	**117.0**	**23.57**	**9.94**	**34.54**
0.28	118.5	23.88	9.67	34.79
0.29	120.4	24.26	9.42	35.17
0.30	124.5	25.08	9.10	36.08
0.31	129.3	26.05	8.80	37.27
0.32	140.0	28.20	8.41	40.01

Figure 52 shows the comparison of equivalent work for all the cases, with each line representing particular value of rich loading.

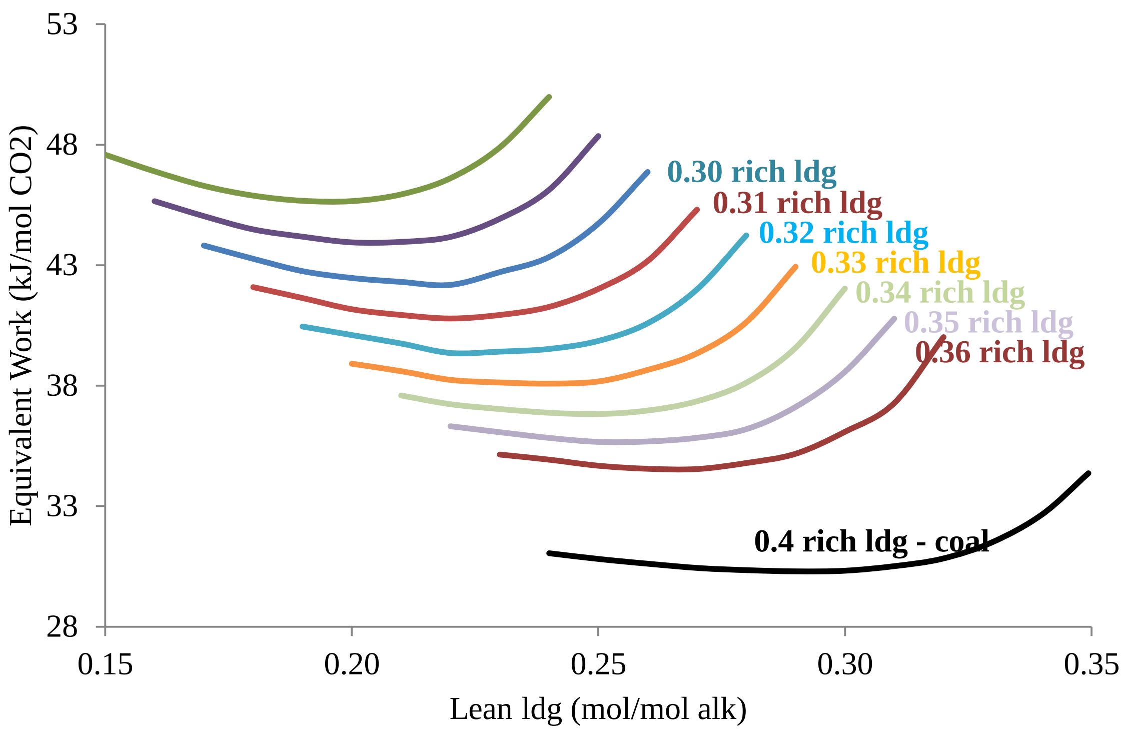

Figure 52: Equivalent Work for various values of rich and lean loadings (8m PZ, 150C stripper, 5C LMTD cross exchanger and interheater, Fawkes model, Mellapak 250X packing)

5.4 CONCLUSIONS

- Equivalent work of 40.5, 38.3, and 37.6 kJ/mol CO_2 is expected for 3%, 6%, and 9% CO_2 cases investigated for low capex configurations, respectively.
- Equivalent work of 34.9, 33.1, and 31.6 kJ/mol CO_2 is expected for 3%, 6% and 9% CO_2 cases investigated for high capex configurations, respectively.
- Best energy performance of 31.6 kJ/mol CO_2 was achieved for high capex scenario of 9% CO_2 case. This was closest to coal combustion case for same configuration which has equivalent work of 30 kJ/mol.
- Sensitivity Analysis shows a 3% decline in energy requirement (opex) for every 0.1 decline in rich loading.
- There is an average 12% improvement in energy performance for high capex case over low capex.
- Carbon capture from combined cycle required 18% more energy than carbon capture from coal combustion.

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